6 DATA ANALYSIS IN SUPPORT OF THE CONCEPTUAL MODEL FOR COPPER AND NICKEL

It is important to supplement the conceptual model discussion provided in the first six sections of this report with data that characterize the components presented in those sections. So doing helps to provide a firm basis for understanding the specific system that is being evaluated, and to determine the adequacy (or limitations) of the data available for calculating TMDLs.

6.1 Overview of Database

The database contained in the conceptual model geographic information system is summarized in Table 6-1. The table is organized by category, source of data, period of record, and comments. As illustrated by the table, a variety of data types are required to understand the processes that influence the fate of copper and nickel. The data gathering efforts have focused on information relevant to the development of TMDLs. A variety of sources were used, as shown by Table 6-1. Approximately two million records were entered. All the data in the database were available in electronic format.

Although rigorous characterization of the San Francisco Bay's hydrodynamics and water quality began about thirty years ago by the USGS, the data in the database emphasizes the most recent 10 to 15 years. This period is coincident with the period of availability of most water and sediment quality data.

6.2 Distribution of Copper and Nickel in Lower South San Francisco Bay, and in Surrounding Waters

In this section, concentrations of copper and nickel in the water column (total and dissolved), in the bedded sediments, in bivalve tissues, and in point source discharges are summarized. That information is presented in Figures 6-1 through 6-8, and in Tables 6-2 through 6-6, and is described below. Note that in a number of the figures, such as Figure 6-1, which display bar charts where a number of the bars are clustered over the Lower South San Francisco Bay, part of the figure is magnified for clarity. Also included are locations of the three wastewater discharges.

Figures 6-1 and 6-2 illustrate the total and dissolved copper concentrations in the water column and total and dissolved nickel concentrations in the water column, respectively, at locations throughout the San Francisco Bay. The plotted values are averages of the data collected at each location shown, using the SFEI data. Tables 6-2 through 6-5 contain the actual data, as well as supplementary statistics (such as minimum and maximum values). The figures exhibit great similarities with respect to each other. Highest concentrations of copper and nickel are typically present in Lower South San Francisco Bay (total copper concentrations can exceed 10 μg/L, and total nickel concentrations can exceed 20 μg/L), followed by locations in the North Bay. Concentrations decrease in Central South San Francisco Bay, in Central Bay, and are lowest of all in the Pacific Ocean near the Golden Gate, typically less than 1μg/L.

Figures 6-3 and 6-4 show total copper and total nickel concentrations, respectively, during the dry and wet seasons. The dry season is defined to be June through October, and the wet season is defined to be December through April. In North San Francisco Bay, wet season concentrations are clearly higher for copper and nickel; in the central and northern South San Francisco Bay, concentrations are comparable during the two seasons, while in Lower South San Francisco Bay dry season concentrations are the highest.

Sediment copper and sediment nickel concentrations throughout the Bay are shown in Figure 6-5a. The concentrations are averages of the data for each location. Selected statistics of the data are provided in Table 6-6. Sediment nickel concentrations range from about 65 to 110 mg/kg and are about twice as high as sediment copper concentrations (20 to 60 mg/kg) at most locations. In contrast to water column concentrations, the sediment metal concentrations are more uniform throughout the Bay. Concentrations in central South San Francisco Bay are somewhat lower than elsewhere, as they were for water column concentrations. The sediment concentrations at each location are relatively constant, as noted by the small standard deviations in the data (see Table 6-6).

The sediment concentration data presented in Figure 6-5a are surface sediment concentrations (sediments collected within 5 cm of the sediment-water interface). Few sediment core data for South San Francisco Bay area have been located, and such data do not appear to be widely available. The data available in the database for South San Francisco Bay have been plotted and are shown in Figure 6-5b. The top graph in the figure shows copper and nickel concentrations taken about one kilometer south of the San Mateo Bridge in South San Francisco Bay. Also shown in that figure are sediment core data from a Tomales Bay sample, a location with minimal anthropogenic impact. The Tomales Bay copper core result portrays a fairly constant concentration (20 micrograms per gram [μg/g]) over depth, with a slight enrichment in the top 50 cm. Copper concentrations near the San Mateo Bridge are higher at all depths, and also show an enrichment in concentrations in the top 50 cm. In contrast, sediment nickel concentrations are uniformly higher at the Tomales Bay location. One possible explanation for this could be due to the different geologic formations at the two locations.

In the lower graph in Figure 6-5b, profiles of copper and nickel are shown at two locations in Lower South San Francisco Bay: Mayfield Slough and Coyote Creek. The profiles of copper are similar at the two locations, but the same is not true for nickel, where for most of the depth profile nickel concentrations are higher in Coyote Creek. Note that the Tomales Bay nickel core sample concentrations are higher than, or approximately equal to, nickel concentrations at both South San Francisco Bay locations.

Only a small amount of sediment quality data is available in the upland watershed for Lower South San Francisco Bay with which to compare to these in-Bay sediment quality data. The following background soils data, based on upland sediment concentrations from Calabazas Creek, were included in the copper and nickel source characterizations report (Tetra Tech, 1998b):

copper	38.6 mg/kg
nickel	81.6 mg/kg

The copper concentration is near the maximum of the concentrations previously shown in Figure 6-5b, while the nickel concentration is near the minimum of those concentrations.

Concentrations of copper and nickel in bivalves are shown in Figure 6-6 for locations throughout San Francisco Bay. The bivalves sampled were collected by SFEI from uncontaminated sites and transplanted to locations throughout the Bay during the wet season (defined as February through May) and the dry season (defined as June through September). Different species of bivalves were transplanted, according to expected salinity in each deployed area. Near the Coyote Creek station, the oyster *Crassostrea gigas* was transplanted from Tomales Bay Oyster Company. At the remaining South Bay stations, the mussel *Mytilus californianus* was transplanted from Bodega Head.

The average concentrations of the bivalves prior to transplanting was:

	Cu (mg/kg)	**Ni (mg/kg)**
Crassostrea gigas	125.9	4.3
Mytilus californianus	5.6	12.6

The concentrations of copper and nickel in the bivalves at locations in South San Francisco Bay shown in Figure 6-6 are:

Location	**Bivalve**	**Cu (mg/kg)**	**Ni (mg/kg)**
BA10	*Crassostrea gigas*	457	5.5
BA30	*Mytilus californianus*	48	16
BA40	*Mytilus californianus*	8	12
BC10	*Mytilus californianus*	8	11

Increased copper concentrations are present in bivalves at BA10 and BA30, but not at the remaining two South San Francisco Bay stations. Nickel concentrations in the bivalves are near their background values at all four stations.

To compare copper and nickel effluent concentrations in the three POTWs that discharge to Lower South San Francisco Bay with water column concentrations, Figure 6-7a has been prepared for copper, and Figure 6-7b has been prepared for nickel. Those plots compare total concentrations in the effluents of the POTWs to total water column concentrations at locations within Lower South San Francisco Bay, including in several sloughs. Figure 6-7c shows locations of sampling stations for three WWTPs in Lower South San Francisco Bay. While effluent copper and nickel concentrations from the point sources have either decreased over time, or remained practically constant, the concentrations in the Bay appear to have remained constant, subject to seasonal scatter. It is also noted that concentrations of both copper and nickel have, at times, been higher than in the wastewater that is discharged into the sloughs.

Because of the apparent similarities in water column copper and nickel concentrations discussed earlier, a correlation between total water column concentrations has been prepared, and is shown in Figure 6-8. The locations plotted are located throughout South San Francisco Bay north to the Bay Bridge. The single station with outlier data is labeled, and is near the Palo Alto shoreline.

Due to the higher total concentrations of copper and nickel in Lower South San Francisco Bay than elsewhere, Figures 6-9a and 6-9b have been prepared to show that the average spatial distribution of total suspended solid (TSS) concentrations throughout the bay. The highest concentrations of TSS correspond to Lower South San Francisco Bay, not unexpected due to the shallow depths and wetting/drying there. Average concentrations range from 20 mg/L to over 100 mg/L. Those concentrations rapidly decrease in the central portion of South San Francisco Bay, where average concentrations are typically below 10 mg/L. A second general location where suspended solids are high is in the northern portion of San Francisco Bay.

Shown in Figures 6-9c and 6-9d are ratios of total to dissolved concentrations for copper and nickel. Those ratios are higher where TSS is higher, indicating the importance of the relationship between TSS and total metal concentrations. Also, the ratios are higher for nickel than for copper by about 30 to 50 percent, indicating that nickel has a higher affinity for particulates.

6.3 Meteorological Influences

Annual precipitation rates at four locations around the Bay Area are shown on Figure 6-10a. Those stations are at San Francisco Airport, San Jose Airport, Tracy pumping station, and on Black Mountain (Figure 6-10b). Also shown on the time series are the long-term precipitation averages, which are as follows:

- San Francisco Airport: 19.9 inches/year (from 1948 to 1997)
- San Jose: 14.2 inches/year (from 1948 to 1997)
- Black Mountain (elevation of 2,120 ft mean sea level): 34.9 inches/year (from 1954 to 1995)
- Tracy Pumping plant: 12.5 inches/year (from 1984 to 1998)

The Black Mountain station was chosen to illustrate the influence of topography on precipitation within the watershed (none of the other stations are at elevated locations). At the Black Mountain station, the annual average precipitation is about twice that at the other stations. The period of record examined in Figure 6-10a illustrates both wet and dry years compared with long-term averages. The Tracy pumping station was chosen as one of the four stations because that was the only station at which daily values of evaporation were reported.

Since the precipitation data in Figure 6-10a are yearly averages, patterns of precipitation within a year cannot be seen. One year (1994) was selected to show that comparison. Those results are plotted in Figure 6-10c, and the presence of dry and wet seasons is evident. Practically no precipitation fell for four consecutive months (June to October).

To show the comparison between precipitation and evaporation over the course of a year, Figure 6-11 has been prepared. Note that evaporation is highest during the dry season (over 0.5 inches/day). This is significant for Lower South San Francisco Bay since natural surface water inflows are minimal during this time of the year, so that evaporation of water from the surface of the Bay can reduce the beneficial flushing effects of remaining freshwater discharges.

6.4 Hydrological Influences

This section provides a brief overview of the freshwater inflow rates into San Francisco Bay from the Delta and from sources that discharge directly into Lower South San Francisco Bay. Delta inflow rates over the past 10 years are shown in Figure 6-12a. That figure demonstrates the year-to-year variability of flow rates through the Delta. For some years, the peak inflow rates are 1,000 to 2,000 m^3/s, while for other years, peak inflow rates can exceed 10,000 m^3/s. In comparison, stream inflow rates for the Guadalupe River, which discharges into Lower South San Francisco Bay, is shown in Figure 6-12b. The location of that station is shown in Figure 6-12c. Note that these discharge rates are several orders of magnitude less than the Delta discharge rates. Since the Guadalupe River station comprises about 25 percent of the Lower South San Francisco Bay drainage area, the total discharge rate from the local watershed is approximately four times that shown in the figure, and is still very small compared to the Delta discharges.

In Figure 6-13, the volumetric discharges from the wastewater treatment plants are shown for a period of four years. The San Jose/Santa Clara plant discharge exceeds the sum of the other two discharges combined. Although day-to-day changes in volumetric discharges are apparent, the discharges remain fairly uniform from season to season, compared with natural stream inflows. During the dry season, it is apparent that wastewater discharges can exceed natural stream flows.

6.5 Hydrodynamic Data for Lower South San Francisco Bay

This discussion of hydrodynamic data focuses on total suspended solids, water surface elevations due to tidal effects, water velocities at several locations in the Bay, and seasonal salinity changes. At certain locations, these data have been collected over very short time intervals (on the order of minutes). A number of these data sets are discussed below.

In Figure 6-14, time series of suspended solids concentrations at three South San Francisco Bay locations are shown for one week in August 1993. At each location, sensors are used to estimate suspended sediment concentrations at two depths: typically mid-depth and near the bottom. Note that concentrations decrease dramatically from Channel Marker 17 (in Lower South San Francisco Bay) to the Bay Bridge (near Central San Francisco Bay). Maximum concentrations at Channel Marker 17 exceed 1,000 mg/L on a nearly daily basis. At the Bay Bridge, concentrations are not as temporally variable, and seldom exceed 50 mg/L. Further, it is noted that at Channel Marker 17, concentrations are noticeably higher at the deeper of the two sensors. However, at the Dumbarton Bridge, the concentrations at the deeper sensor are only slightly higher than at the shallow sensor. At the Bay Bridge, the difference is even smaller. These results suggest that vertical concentration gradients of suspended solids are not great north of Lower South San Francisco Bay, and that deposition of larger size fractions of suspended solids may be occurring over distance.

In Figure 6-15, tidal elevations are compared at two locations in South San Francisco Bay: at the Bay Bridge and at the Dumbarton Bridge. The semi-diurnal nature of the tides is evident at both stations, as well as the continuing evolution period of the tides over the one week examined. Also, tidal amplification is evident at the Dumbarton Bridge when compared with the Bay Bridge, as discussed previously, as a result of the standing wave phenomenon associated with South San Francisco Bay.

Examples of tidal speeds are shown in Figure 6-16 for a one-week period in late May and early June 1980. Note that the maximum speeds are greater at the location south of the Dumbarton Bridge. There, tidal speeds routinely exceed 50 to 60 centimeters per second (cm/s) during a portion of the tidal cycle, while maximum speeds near the Bay Bridge are typically less by about 10 cm/s.

The time variation of salinity at three locations in South San Francisco Bay over a period of five years is illustrated in Figure 6-17. Note the dramatic salinity changes from dry to wet season each year, in response to freshwater inflows. Also, salinity is generally lower with increasing distance away from the Bay Bridge into South San Francisco Bay, a consequence of local freshwater discharges into South San Francisco Bay.

The relationship between copper, nickel and salinity is shown in Figure 6-18a, and the locations are illustrated in Figure 6-18b. Note that the concentrations of both copper and nickel decrease uniformly with increasing salinity. This relationship suggests that at least part of the reason that copper and nickel concentrations decrease within the South Bay (with respect to BA10 to BB70) is due to dilution with ocean water.

6.6 Summary

1. A database has been developed to support the conceptual model development for copper and nickel in Lower South San Francisco Bay.

2. The database has been utilized throughout this report. In this section the database was used to illustrate: distribution of copper and nickel in Lower South Bay, meteorological influences, hydrological influences, and hydrodynamic influences.

3. Specific results shown in this section include:

    - The water column copper and nickel concentrations are spatially variable, and decrease fairly uniformly from Lower South Bay up through Central South Bay.
    - While temporal variability in dissolved copper and nickel concentrations exist, those concentrations appear to be buffered, at least to some degree, in the Lower South Bay.
    - Sediment copper and nickel concentrations are not as spatially variable as water column concentrations.
    - A few sediment core copper and nickel concentrations are available (near the San Mateo Bridge and in Tomales Bay), and appear to show that sediment copper concentrations in Lower South Bay are elevated, while such a conclusion for nickel is not as clear.

- Concentrations of copper in transplanted bivalves in Lower South Bay near stations BA10 and BA30 appear elevated relative to concentrations prior to transplanting. No such elevated concentrations are seen for nickel.
- Long-term precipitation rates are spatially variable throughout the San Francisco Bay area, and also show variability with altitude.
- Due to the small watershed that drains the Lower South Bay, and due to seasonal precipitation patterns, surface water discharges directly into the Lower South Bay typically occur only during the wet season, and vary considerably from year to year.
- Suspended particulate concentrations in Lower South Bay can vary significantly with depth, and concentrations as high as 1000 mg/l have been observed.
- Tidal amplification in Lower South Bay is evident relative to the tides at the Golden Gate.
- Tidal speeds in the Lower South Bay can typically exceed 50 to 60 cm/sec.
- During the dry season, an approximate balance occurs between POTW discharges and evaporation.

Table 6-1
Status of Data for GIS Database for Conceptual Model of Copper and Nickel in Lower South San Francisco Bay

CATEGORY	SOURCE	PERIOD OF RECORD	COMMENTS
Water Quality Data-I	San Francisco Estuary Institute (SFEI); South Bay Dischargers Association; SFEI Pilot Study; Special Palo Alto study	1989-1997	The water quality data consist of Cu, Ni, and many water quality indicators at locations throughout San Francisco Bay.
Water Quality Data-II	City of San Jose	1997-1998	Data consist of Cu and Ni in the Lower South Bay.
Sediment Quality Data-I	SFEI	1994-1997	The sediment quality data consist of near-surface sediment Cu and Ni concentrations, and many other sediment quality indicators at locations throughout San Francisco Bay.
Sediment Quality Data-II	Bay Protection and Toxic Clean-up Program: Moss Landing Marine Labs	1994-1997	Copper and nickel at locations throughout the Bay
Copper in sediments: 1970 study	USGS	1970	Data included for reference only
Bivalve Tissue Data	SFEI	1993-1996	These data consist of Cu and Ni concentrations in bivalves placed at different locations throughout San Francisco Bay; also included are Cu and Ni concentrations in the bivalves at their native locations.
Long-term sediment and bivalve study near Palo Alto	USGS	1977-1997	Have USGS report, but not electronic data
State mussel watch data		1990's	Not presently input due to small amount of data in study area
Bathymetry I	Stanford University; USGS	Multiple bathymetric surveys	Detailed bathymetric data are available for South San Francisco Bay from Stanford University that has been used for hydrodynamic modeling.
Bathymetry-II (of extreme Lower South Bay)	USGS and RWQCB	1990's	Have data on diskette
Point Source Discharge Data-I	Individual Point Sources	1988-1998	The data include Cu, Ni, TSS, and flow rate information in effluent of four individual point sources that discharge into South San Francisco Bay.

Table 6-1 (continued)
Summary of Data for GIS Database for Conceptual Model of Copper and Nickel in Lower South San Francisco Bay

CATEGORY	SOURCE	PERIOD OF RECORD	COMMENTS
Point Source Discharge Data-II	Individual Point Sources in South Bay north of Dumbarton Bridge	1988-1998	Data not yet in format for entry.
Nonpoint Source Data	Source Characterization Report(1998)	Various periods by source type	Presently a lower priority; not yet done
Surface Water Inflow Rates: South Bay	USGS	1903-1997 (not continuous for all stations)	These data include the major streams that discharge into Lower South San Francisco Bay, plus Alameda Creek.
Streams: Delta Composite Index-I	USGS	1988-1997	These data are the Delta volumetric discharge flow rates for the most recent 10 years.
Delta Index-II	USGS	1986-1987	Add wet year to database; not yet entered.
Meteorology-I	National Climatic Data Center	1948-1998 (not continuous for all stations)	Meteorological data for stations around the Bay Area.
Meteorology-II	Moffett Field	Probably last 10 years	Availability of data presently being investigated.
Water Levels at locations in South San Francisco Bay	USGS	1979-1984	These are continuous water level data at discrete locations for different periods of time.
Total Suspended Solids in San Francisco Bay	USGS	1991-1996	These data are suspended solids concentrations collected at 15-minute time intervals; concentrations are available at locations throughout the Bay; concentrations are typically measured at two depth intervals. Also, monthly vertical profiles of suspended solids data for 1994-1996 at locations around the Bay
Current meter data, and related hydrodynamic information	USGS	1979-1984	Data include current speed, direction, and various other data types (water temperature, salinity).
Geologic map of San Francisco Bay Area	USGS	–	Scanned into database; geologic layers being added
Aerial Photographs	City of San Jose	Recent years	Not yet obtained
Background Cu and Ni concentrations in upland soils	Watershed Management Initiative	unknown	Very few data available; not yet acquired.
Copper and Nickel speciation data in South Bay	D. Sedlak at UCB	1997	Data available in peer reviewed literature.

Table 6-2
Selected Statistics of Total Copper Concentrations (all units μg/L) at Locations Throughout San Francisco Bay

Station	Sample Size	Minimum	Maximum	Mean	Median	UCL95*	Standard Deviation
PA+STATION1	14	3.4	9.9	5.76429	4.85	6.75233	2.08755
PA+STATION2	14	4.1	11	5.75	4.95	6.64201	1.88465
PA+STATION3	12	4.9	16	8.05833	6.6	9.75969	3.28176
PA+STATION4	12	3.8	9.6	5.475	4.8	6.46215	1.90412
SBDA+C-1-0	21	3.2	7.5	5.31429	5.4	5.7829	1.2451
SBDA+C-1-1	19	2.3	8.6	5.18947	5.3	5.88093	1.7381
SBDA+C-1-3	20	4.9	25.6	13.26	14.3	15.9555	6.97148
SBDA+C-2-0	12	2.4	30	6.825	4.35	10.7384	7.54865
SBDA+C-2-5	13	4.8	18.2	8.84615	6	11.1525	4.66576
SBDA+C-3-0	18	4.9	22.1	10.0722	7.1	12.3657	5.59346
SBDA+C-5-0	12	4.3	14	7.375	6.55	8.94032	3.01937
SBDA+C-6-0	16	4.1	16	8.63125	7.95	10.2143	3.61215
SBDA+C-X	12	6	18.2	12.1333	12	13.9821	3.56609
SBDA+R-2	13	5.1	16	8.53846	6.6	10.2828	3.52882
SBDA+R-4	18	5.2	23	10.5667	9.25	12.611	4.98586
SBDA+R-5	15	5.2	17	8.4	8.5	9.76127	2.99333
SBDA+SB-4	13	3.4	9.6	5.40769	4.7	6.30259	1.81037
SBDA+SB-5	18	3.4	9.1	5.18333	4.6	5.90145	1.75139
SBDA+SB-6	12	3.8	12	6.10833	5.4	7.32002	2.33723
SBDA+SB-7	18	3.4	10	5.25	5.2	5.87663	1.52826
SFEI+BA10	12	3.08	11.79	5.89058	5.5955	7.1589	2.44648
SFEI+BA20	15	2.97	6.347	4.53927	4.526	5.01648	1.04936
SFEI+BA30	15	2.98	7.19	4.3002	3.886	4.85768	1.22586
SFEI+BA40	15	2.16	4.327	3.1138	2.99	3.38823	0.603443
SFEI+BB15	11	1.723	3.96	2.82291	2.78	3.20143	0.692654
SFEI+BB30	15	1.241	3.192	2.1236	2.15	2.41824	0.647898
SFEI+BB70	12	1.23	3.253	2.04833	1.9645	2.32737	0.538242
SFEI+BC10	15	1.24	2.45	1.82647	1.8	1.98832	0.355893
SFEI+BC20	14	0.19	1.315	0.621786	0.59	0.750062	0.271025
SFEI+BC30	15	1.346	2.41	1.73573	1.57	1.89465	0.349447
SFEI+BC41	15	1.16	4.17	1.92793	1.732	2.25196	0.712504
SFEI+BC60	12	1.167	3.552	2.01608	1.707	2.42663	0.791906
SFEI+BD15w	3	4.002	12.422	8.57133	9.29	15.7459	4.25576
SFEI+BD20	3	2.2	6.882	4.92767	5.701	9.03258	2.43492
SFEI+BD30	3	1.86	10.348	5.179	3.329	12.8266	4.53634
SFEI+BD40	3	3.829	7.391	5.31133	4.714	8.43793	1.85461
SFEI+BD50	3	3.921	9.826	6.42933	5.541	11.573	3.05108
SFEI+BF10	3	4.41	7.554	5.88967	5.705	8.55351	1.58011
SFEI+BF20	3	1.665	9.499	5.523	5.405	12.1287	3.91833
SFEI+BF40	3	3.436	10.884	8.01133	9.714	14.7637	4.00531
SFEI+BG20	3	2.219	9.864	5.15233	3.374	12.0999	4.12109
SFEI+BG30	3	2.359	4.756	3.303	2.794	5.45583	1.27699
SFEI+C-1-3	12	3.523	14.412	7.029	6.702	8.65403	3.13453
SFEI+C-3-0	12	4.177	13.045	8.49708	8.2215	10.2631	3.40652
SJ+CC	25	3.05	13.1	6.9348	6.6	7.85366	2.68533
SJ+DBN	25	2.38	11.3	4.3184	4	4.97187	1.90975
SJ+DBS	25	2.66	13.5	4.8068	4.1	5.53099	2.11642
SJ+SM	8	2.1	8.5	3.4	2.8	4.8014	2.09216

* UCL95 = 95th percent upper confidence level of mean.

Table 6-3
Selected Statistics of Dissolved Copper Concentrations (all units µg/L) at Locations Throughout San Francisco Bay

Station	Sample Size	Minimum	Maximum	Mean	Median	UCL95*	Standard Deviation
PA+STATION1	14	1.4	6.3	3.35714	3.15	3.90901	1.166
PA+STATION2	14	1.7	6.8	3.95	4.05	4.72522	1.63789
PA+STATION3	12	2.3	16	6.09167	5.3	7.89196	3.47261
PA+STATION4	12	1.3	7.6	4.15833	3.85	5.01233	1.64729
SBDA+C-1-0	21	2.9	6.4	4.4381	4.4	4.78803	0.929772
SBDA+C-1-1	19	1.4	6.5	3.12105	3.2	3.66192	1.35957
SBDA+C-1-3	20	2.5	8.9	4.3	3.6	5.08591	2.03263
SBDA+C-2-0	12	1.4	6.7	3.14167	2.9	3.94889	1.55707
SBDA+C-2-5	13	3.1	6.8	4.34615	4.1	4.85971	1.03892
SBDA+C-3-0	18	2.5	9.4	4.15	3.65	4.85534	1.72021
SBDA+C-5-0	12	3	7.3	4.21667	3.75	4.94476	1.40443
SBDA+C-6-0	16	3	7.9	4.04375	3.6	4.61202	1.29665
SBDA+C-X	12	3.5	7.3	4.48333	4.2	5.05631	1.10522
SBDA+R-2	13	2.7	7.4	4.00769	3.6	4.61995	1.23859
SBDA+R-4	18	2.6	6.8	3.91111	3.7	4.38719	1.16108
SBDA+R-5	15	2.3	7.6	4.21333	3.8	4.87968	1.46525
SBDA+SB-4	13	1.4	6.3	3.36154	3.1	3.91624	1.12215
SBDA+SB-5	18	2.2	6.5	3.47778	3.2	3.90449	1.04068
SBDA+SB-6	12	2.2	7	3.90833	3.55	4.60122	1.33652
SBDA+SB-7	18	2.3	6.6	3.67222	3.45	4.13735	1.13439
SFEI+BA10	12	1.608	4.89	3.41525	3.215	3.9262	0.985574
SFEI+BA20	15	1.821	4.956	3.09013	2.951	3.47807	0.853039
SFEI+BA30	15	1.904	3.74	2.82353	2.795	3.0909	0.587919
SFEI+BA40	15	1.418	3.288	2.26873	2.32	2.48214	0.469265
SFEI+BB15	12	1.362	2.96	2.015	2.0295	2.26736	0.486785
SFEI+BB30	15	1.034	2.701	1.62827	1.64	1.85045	0.488571
SFEI+BB70	12	0.987	2.307	1.63983	1.5835	1.84265	0.391217
SFEI+BC10	15	0.96	1.94	1.33633	1.241	1.46148	0.275195
SFEI+BC20	15	0.2	0.999	0.4832	0.423	0.595161	0.246194
SFEI+BC30	15	0.715	1.91	1.16573	1.04	1.32743	0.355559
SFEI+BC41	15	0.929	2.009	1.30267	1.189	1.45092	0.326002
SFEI+BC60	12	0.581	2.144	1.28358	1.2695	1.50045	0.41832
SFEI+BD15w	3	2.338	4.162	3.35133	3.554	4.91705	0.928735
SFEI+BD20	3	1.191	1.735	1.51767	1.627	2.00321	0.288009
SFEI+BD30	3	1.457	1.513	1.48833	1.495	1.53653	0.028589
SFEI+BD40	3	1.277	2.326	1.74433	1.63	2.64418	0.533764
SFEI+BD50	3	1.298	1.957	1.588	1.509	2.15534	0.336528
SFEI+BF10	3	1.456	2.302	1.86067	1.824	2.57579	0.42419
SFEI+BF20	3	1.827	2.828	2.18333	1.895	3.12629	0.559332
SFEI+BF40	3	1.455	2.086	1.754	1.721	2.28806	0.316792
SFEI+BG20	3	1.314	2.044	1.60867	1.468	2.25737	0.384793
SFEI+BG30	3	1.457	1.857	1.65667	1.656	1.99384	0.200001
SFEI+C-1-3	12	1.38	4.804	2.79233	2.518	3.39807	1.16841
SFEI+C-3-0	12	1.634	5.929	3.35367	3.434	3.95358	1.15719
SJ+CC	25	1.97	4.1	3.0712	3.03	3.28332	0.619922
SJ+DBN	25	1.4	3.7	2.5136	2.5	2.71396	0.585547
SJ+DBS	25	1.68	3.7	2.6768	2.67	2.85213	0.51241
SJ+SM	8	1.6	2.2	1.9125	1.85	2.06624	0.229518
UCSC+1	3	2.73222	4.63842	3.89712	4.32072	5.61882	1.02126
UCSC+10	3	0.54009	1.08018	0.87897	1.01664	1.37662	0.295193
UCSC+11	3	0.552798	1.20726	0.967926	1.14372	1.57637	0.360912
UCSC+2	3	2.73222	4.00302	3.30408	3.177	4.39122	0.644861
UCSC+3	3	2.28744	3.30408	2.8593	2.98638	3.73611	0.520097
UCSC+4	3	2.2239	2.5416	2.4357	2.5416	2.74493	0.183424
UCSC+6	3	1.96974	2.35098	2.20272	2.28744	2.54706	0.204253
UCSC+9	3	1.2708	1.33434	1.29198	1.2708	1.35383	0.0366848
USCS+5	3	2.09682	2.92284	2.58396	2.73222	3.31311	0.432508
USCS+7	3	1.84266	2.28744	2.13918	2.28744	2.5721	0.256794
USCS+8	3	1.39788	2.03328	1.63086	1.46142	2.22083	0.349951

* UCL95 = 95th percent upper confidence level of mean.

Table 6-4
Selected Statistics of Total Nickel Concentrations (all units μg/L)
at Locations Throughout San Francisco Bay

Station	Sample Size	Minimum	Maximum	Mean	Median	UCL95*	Standard Deviation
PA+STATION1	14	3.7	22	7.75714	6.15	10.1391	5.03262
PA+STATION2	14	4.4	12.2	6.85714	6.3	7.9216	2.249
PA+STATION3	12	4.3	9.4	6.41667	5.85	7.40027	1.89729
PA+STATION4	12	4.2	12	6.24167	5.5	7.36308	2.1631
SBDA+C-1-0	21	8.8	25	13.5571	13	14.9515	3.7048
SBDA+C-1-1	19	6.2	15.3	10.8895	11	11.8603	2.44038
SBDA+C-1-3	20	7.2	48	22.12	21	26.8015	12.108
SBDA+C-2-0	12	6.4	58	15.0083	10.7	22.2474	13.9634
SBDA+C-2-5	13	10	28	17.8615	16	21.0164	6.38234
SBDA+C-3-0	18	10	38	17.8222	17	21.2028	8.24468
SBDA+C-5-0	12	5.9	23	12.2667	10.8	14.8107	4.9072
SBDA+C-6-0	16	6.1	24.2	13.8937	13.5	16.6513	6.29195
SBDA+C-X	12	13	32	23.525	23.25	26.4828	5.70536
SBDA+R-2	13	6.9	27	14.3	12.8	17.5419	6.55833
SBDA+R-4	18	7.6	40	18.0611	18.5	21.3359	7.98669
SBDA+R-5	15	8.1	23	14.5733	13	17.0187	5.37726
SBDA+SB-4	13	3.7	15.1	6.53077	5.6	8.05441	3.08231
SBDA+SB-5	18	4.1	22.5	8.18333	6.8	9.98215	4.38705
SBDA+SB-6	12	4.4	16	9.35833	8.05	11.3638	3.86839
SBDA+SB-7	18	4.3	13	8.28333	8.1	9.34971	2.60074
SFEI+BA10	12	4.172	22.31	10.2142	8.7305	12.7972	4.98235
SFEI+BA20	15	3.96	10.694	6.45993	6.25	7.3241	1.90023
SFEI+BA30	15	3.57	13.03	6.01967	4.64	7.21157	2.62091
SFEI+BA40	15	2.5	10.37	4.40873	3.88	5.24974	1.8493
SFEI+BB15	11	2.006	6.21	3.39564	3.222	4.05429	1.20527
SFEI+BB30	15	1.205	4.427	2.48947	2.481	2.89614	0.894237
SFEI+BB70	12	1.045	3.23	2.45525	2.462	2.79184	0.649249
SFEI+BC10	15	1.24	3.213	2.19667	2.289	2.45151	0.560379
SFEI+BC20	15	0.33	1.602	0.829667	0.822	0.98965	0.35179
SFEI+BC30	15	1.385	2.765	2.00273	1.96	2.18873	0.408986
SFEI+BC41	15	1.09	7.31	2.6088	2.26	3.27413	1.463
SFEI+BC60	12	1.28	5.036	2.60575	2.1525	3.20639	1.15858
SFEI+BD15w	3	5.554	39.482	20.3403	15.985	49.6376	17.3783
SFEI+BD20	3	3.127	22.87	11.8887	9.669	28.8432	10.0569
SFEI+BD30	3	2.537	19.643	9.27667	5.65	24.6372	9.11144
SFEI+BD40	3	6.281	12.837	9.158	8.356	14.8069	3.35077
SFEI+BD50	3	5.544	21.258	12.1073	9.52	25.8812	8.17026
SFEI+BF10	3	6.282	16.611	10.918	9.861	19.7603	5.245
SFEI+BF20	3	3.422	20.764	10.9417	8.639	25.9413	8.89736
SFEI+BF40	3	5.484	28.5	16.758	16.29	36.1708	11.5151
SFEI+BG20	3	4.156	21.786	10.1957	4.645	27.1225	10.0405
SFEI+BG30	3	2.729	4.847	3.58567	3.181	5.4662	1.11548
SFEI+C-1-3	12	6.11	36.713	14.6154	11.325	18.9754	8.41008
SFEI+C-3-0	12	3.96	36.03	17.1618	16.2455	21.6542	8.66543

* UCL95 = 95th percent upper confidence level of mean.

Table 6-5
Selected Statistics of Dissolved Nickel Concentrations (all units μg/L) at Locations Throughout San Francisco Bay

Station	Sample Size	Minimum	Maximum	Mean	Median	UCL95*	Standard Deviation
PA+STATION1	14	1.6	5.1	3.2286	2.7	3.75837	1.11936
PA+STATION2	14	2	5.2	3.5571	3.6	4.00796	0.952498
PA+STATION3	12	2.7	6.9	4.4083	4.05	5.0952	1.32491
PA+STATION4	12	1.6	5.5	4.0083	4.2	4.61673	1.17354
SBDA+C-1-0	21	6.2	26	11.067	10	12.6496	4.20587
SBDA+C-1-1	19	2.7	9.5	5.8474	5.6	6.67299	2.07535
SBDA+C-1-3	20	3.9	8.9	6.25	5.35	6.96233	1.84234
SBDA+C-2-0	12	4	11	6.625	6.15	7.66	1.99642
SBDA+C-2-5	13	4.4	15	8.4385	8.6	10.0711	3.30291
SBDA+C-3-0	18	3.3	11	6.2333	5.85	7.17309	2.29193
SBDA+C-5-0	12	3.3	9.3	5.6333	5.2	6.59673	1.85831
SBDA+C-6-0	16	2.7	8.9	5.1875	5.1	5.96836	1.78171
SBDA+C-X	12	3.5	12	7.3083	6.95	8.90156	3.07319
SBDA+R-2	13	2.9	9.2	5.3692	4.5	6.40384	2.093
SBDA+R-4	18	2.8	9	5.0667	4.75	5.78887	1.76135
SBDA+R-5	15	3	9.1	5.26	5	6.21049	2.09004
SBDA+SB-4	13	1.6	5.1	3.1462	2.7	3.67955	1.07905
SBDA+SB-5	18	2.3	9.2	4	3.55	4.65845	1.60587
SBDA+SB-6	12	2.4	11.8	5.4917	4.8	7.03028	2.96785
SBDA+SB-7	18	1.6	10.6	4.6111	4.25	5.39123	1.9026
SFEI+BA10	12	2.093	6.56	4.0686	3.9805	4.65902	1.13891
SFEI+BA20	15	2.37	4.407	3.1803	3.1	3.43066	0.550602
SFEI+BA30	15	2.25	3.42	2.8617	2.882	3.01571	0.338584
SFEI+BA40	15	1.761	3.2	2.3735	2.37	2.55446	0.397848
SFEI+BB15	12	1.4	2.324	1.9225	1.9285	2.08156	0.306808
SFEI+BB30	15	1.01	2.38	1.6422	1.75	1.84188	0.439086
SFEI+BB70	12	1.01	2.192	1.5685	1.57	1.76383	0.376769
SFEI+BC10	15	0.987	2.41	1.4215	1.347	1.6057	0.405122
SFEI+BC20	15	0.31	1.3	0.641	0.54	0.76242	0.266988
SFEI+BC30	15	0.84	1.99	1.1998	1.041	1.36573	0.364866
SFEI+BC41	15	0.973	2.49	1.4041	1.29	1.6172	0.468513
SFEI+BC60	12	0.761	2.22	1.3784	1.228	1.61483	0.456027
SFEI+BD15w	3	2.022	8.267	4.5467	3.351	10.0926	3.28971
SFEI+BD20	3	1.396	2.106	1.823	1.967	2.45733	0.376267
SFEI+BD30	3	1.347	1.734	1.485	1.374	1.84925	0.216062
SFEI+BD40	3	1.152	3.654	2.1877	1.757	4.38841	1.30541
SFEI+BD50	3	1.748	2.513	2.165	2.234	2.81766	0.38714
SFEI+BF10	3	1.167	3.81	2.2187	1.679	4.58175	1.40171
SFEI+BF20	3	1.387	4.528	2.5067	1.605	5.46351	1.75392
SFEI+BF40	3	1.171	2.236	1.8207	2.055	2.78137	0.56986
SFEI+BG20	3	1.005	3.147	1.8193	1.306	3.77425	1.1596
SFEI+BG30	3	0.837	1.888	1.2543	1.038	2.19487	0.557898
SFEI+C-1-3	12	1.576	7.02	4.2976	3.9005	5.18903	1.71952
SFEI+C-3-0	12	2.8	10.936	6.8018	6.7375	7.90019	2.1188
UCSC+1	3	2.64195	4.16841	3.2095	2.81808	4.61736	0.835114
UCSC+10	3	0.5871	1.1742	0.9002	0.93936	1.39839	0.295501
UCSC+11	3	0.64581	1.40904	1.0372	1.05678	1.68119	0.381991
UCSC+2	3	2.11356	3.64002	2.8181	2.70066	4.11614	0.769974
UCSC+3	3	1.99614	2.75937	2.3288	2.23098	2.98785	0.39091
UCSC+4	3	1.58517	2.46582	2.094	2.23098	2.86279	0.456027
UCSC+6	3	1.52646	2.23098	1.9179	1.99614	2.52262	0.358724
UCSC+9	3	1.1742	1.46775	1.3503	1.40904	1.6122	0.155332
USCS+5	3	1.52646	2.52453	2.0744	2.17227	2.92776	0.506179
USCS+7	3	1.52646	2.58324	2.1527	2.3484	3.08819	0.554905
USCS+8	3	1.23291	2.11356	1.6439	1.58517	2.39114	0.443251

* UCL95 = 95th percent upper confidence level of mean.

Table 6-6
Selected Statistics of Sediment Copper and Nickel Concentrations (all units µg/g) in Sufficient Sediments at Locations Throughout San Francisco Bay

Station	Sample Size	Minimum	Maximum	Mean	Median	UCL95*	Standard Deviation
Sediment Copper							
SFEI+BA10	4	24.5	48.939	36.38	36.041	49.0585	10.7746
SFEI+BA21	6	38.3	55.625	45.648	42.6505	51.7958	7.473
SFEI+BA30	6	37.3	48.064	43.037	44.0275	47.0373	4.8626
SFEI+BA41	6	35.388	54.862	43.076	40.3555	48.9729	7.16832
SFEI+BB15	6	27.257	37.602	31.584	31.562	34.5535	3.61017
SFEI+BB30	6	33.154	46.242	37.868	37.0565	41.6749	4.62752
SFEI+BB70	6	36	48.058	41.763	41.7575	45.1568	4.12584
SFEI+BC11	6	25.089	47.696	36.111	35.8515	43.2005	8.61865
SFEI+BC21	6	16.084	38.397	26.452	27.987	33.531	8.60477
SFEI+BC32	6	31.104	38.854	33.98	33.6955	36.2983	2.81829
SFEI+BC41	6	36.4	46.941	40.665	39.5875	43.9061	3.94006
SFEI+BC60	6	7.2	11.118	9.0613	8.873	10.3022	1.50841
SFEI+BD15s	4	49.6	66.665	55.709	53.286	64.8861	7.79894
SFEI+BD22	6	41	54.146	47.952	47.4945	52.016	4.93979
SFEI+BD31	6	35	70.622	53.497	55.7665	64.3856	13.2364
SFEI+BD41	6	17.2	27.333	20.532	19.4305	23.7142	3.86892
SFEI+BD50	6	43.2	68.33	59.867	61.479	67.6029	9.40351
SFEI+BF10	6	14.574	25.6	19.997	19.6915	23.891	4.73359
SFEI+BF21	4	39.8	67.145	57.165	60.858	71.2741	11.9904
SFEI+BF40	6	45.3	71.896	61.492	65.8115	70.2675	10.6675
SFEI+BG20	6	20.715	42.282	28.237	25.163	35.2066	8.47198
SFEI+BG30	6	30.719	47.452	38.141	37.586	42.8606	5.7378
SFEI+C-1-3	6	22.664	94.585	39.95	31.383	62.2909	27.1572
SFEI+C-3-0	6	21.081	57.808	36.719	34.8185	50.3447	16.5638
Sediment Nickel							
SFEI+BA10	4	72.3	116.07	91.843	89.5	114.835	19.5403
SFEI+BA21	6	70.317	117.86	92.427	91.5	105.844	16.3101
SFEI+BA30	6	48.394	103.04	83.307	84.145	99.961	20.2442
SFEI+BA41	6	65.786	103.91	82.147	80.273	93.3423	13.6089
SFEI+BB15	6	45.115	76.732	66.371	68.77	75.5987	11.2175
SFEI+BB30	6	69.31	101.06	81.505	81	91.3957	12.0228
SFEI+BB70	6	63.982	98.19	82.355	81.65	91.8452	11.5359
SFEI+BC11	6	47.527	85.379	68.552	71.803	82.2351	16.6332
SFEI+BC21	6	55.9	79.442	65.973	63.49	74.0348	9.80058
SFEI+BC32	6	64.73	81.052	72.334	73.0765	77.7099	6.53499
SFEI+BC41	6	73.13	91.965	82.547	82.147	87.829	6.42124
SFEI+BC60	6	59.15	73.76	65.705	64.65	69.7643	4.93467
SFEI+BD15s	4	93.6	129.66	110.78	109.935	129.277	15.7171
SFEI+BD22	6	67.373	97.591	81.797	78.65	90.8521	11.0073
SFEI+BD31	6	82.902	117.54	99.27	100.09	111.444	14.7979
SFEI+BD41	6	61.903	80	73.022	73.541	78.2963	6.41168
SFEI+BD50	6	76.5	116.91	98.34	100.095	110.225	14.4481
SFEI+BF10	6	71.9	92.27	80.684	78.4145	87.7425	8.58033
SFEI+BF21	4	68.3	115.35	97.793	103.76	123.966	22.2434
SFEI+BF40	6	85.8	124.56	106.3	107.43	117.891	14.088
SFEI+BG20	6	83.07	113.18	96.152	95.045	106.013	11.987
SFEI+BG30	6	52.6	79.182	65.894	64.718	74.639	10.6308
SFEI+C-1-3	6	57.9	130.82	81.392	77.3525	102.697	25.8977
SFEI+C-3-0	6	68.562	129.8	100.05	102.576	119.273	23.3685

* UCL95 = 95th percent upper confidence level of mean.

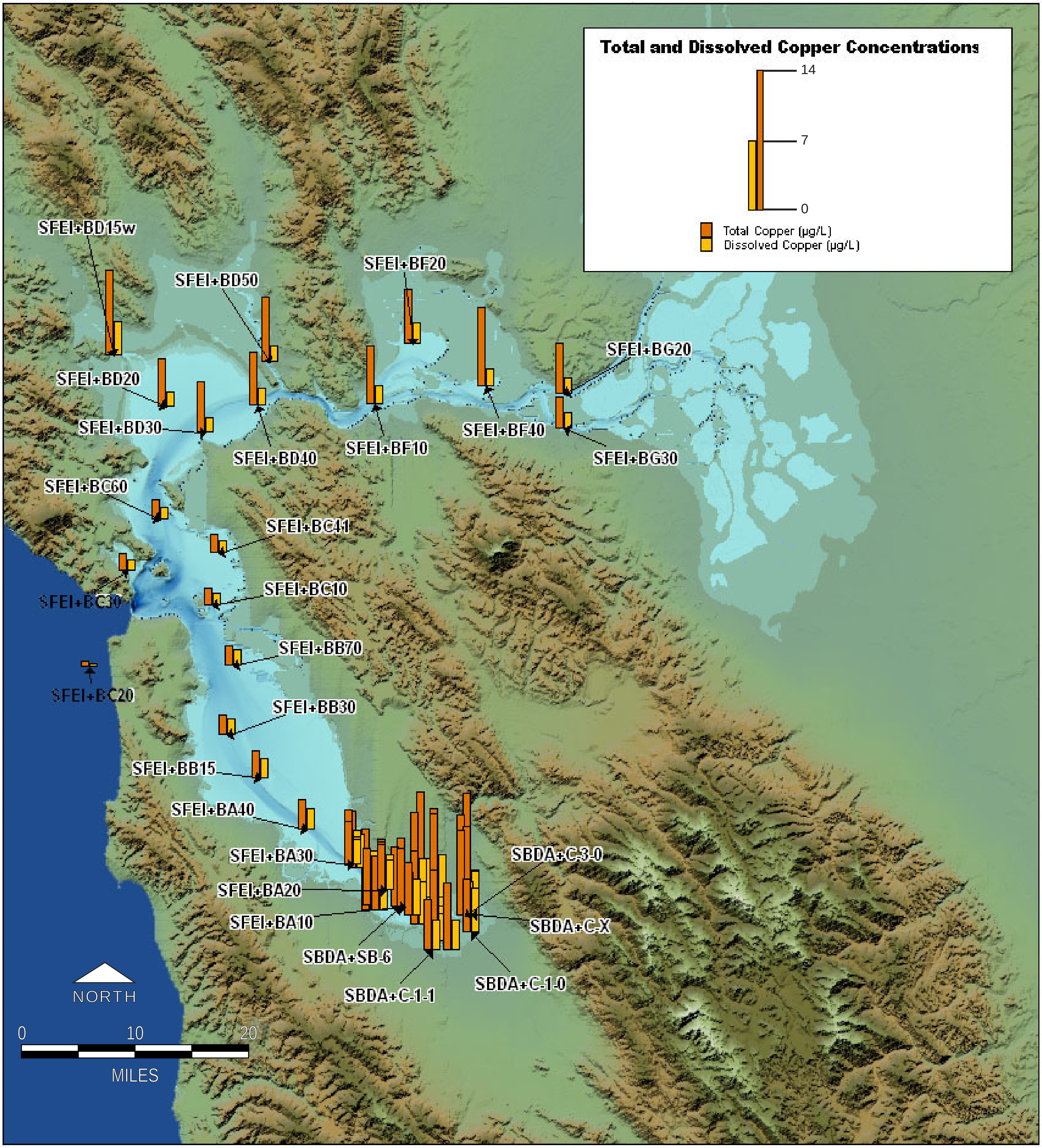


Figure 6-1a. Average total and dissolved copper concentrations in water column at locations throughout San Francisco Bay (1993-1997 data).

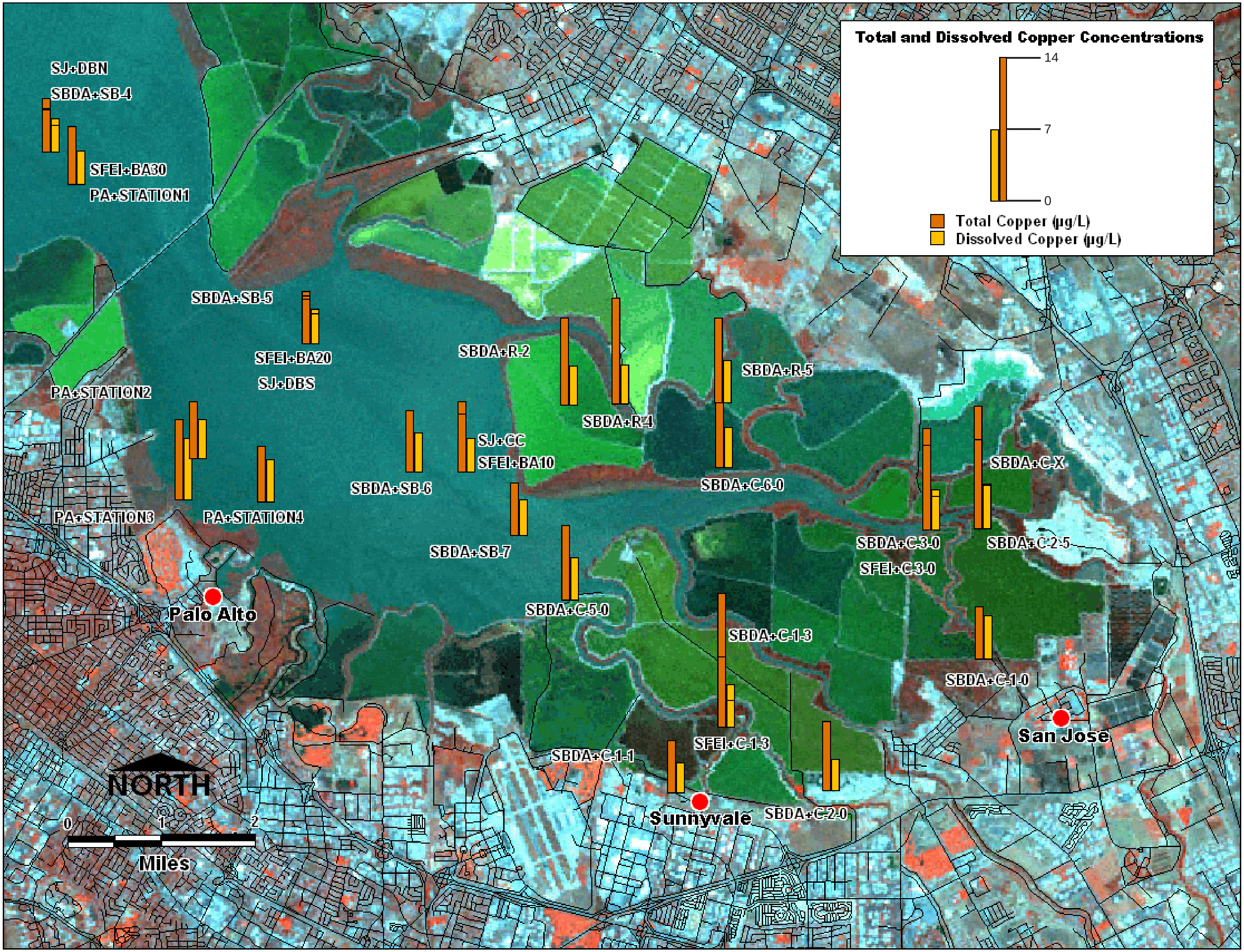


Figure 6-1b. Average total and dissolved copper concentrations in water column at locations throughout Lower South San Francisco Bay.

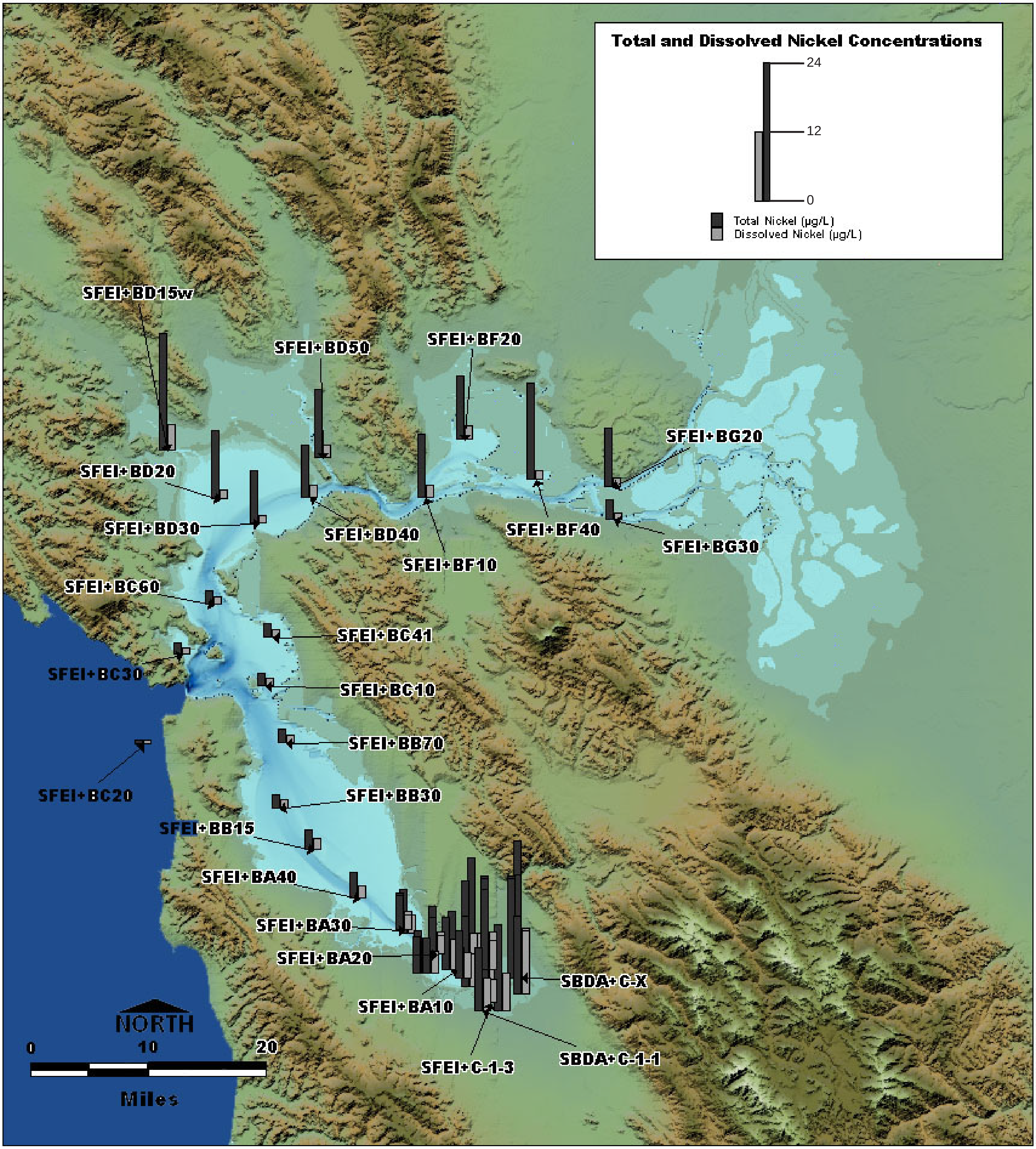


Figure 6-2a. Average total and dissolved nickel concentrations in water column at locations throughout San Francisco Bay.

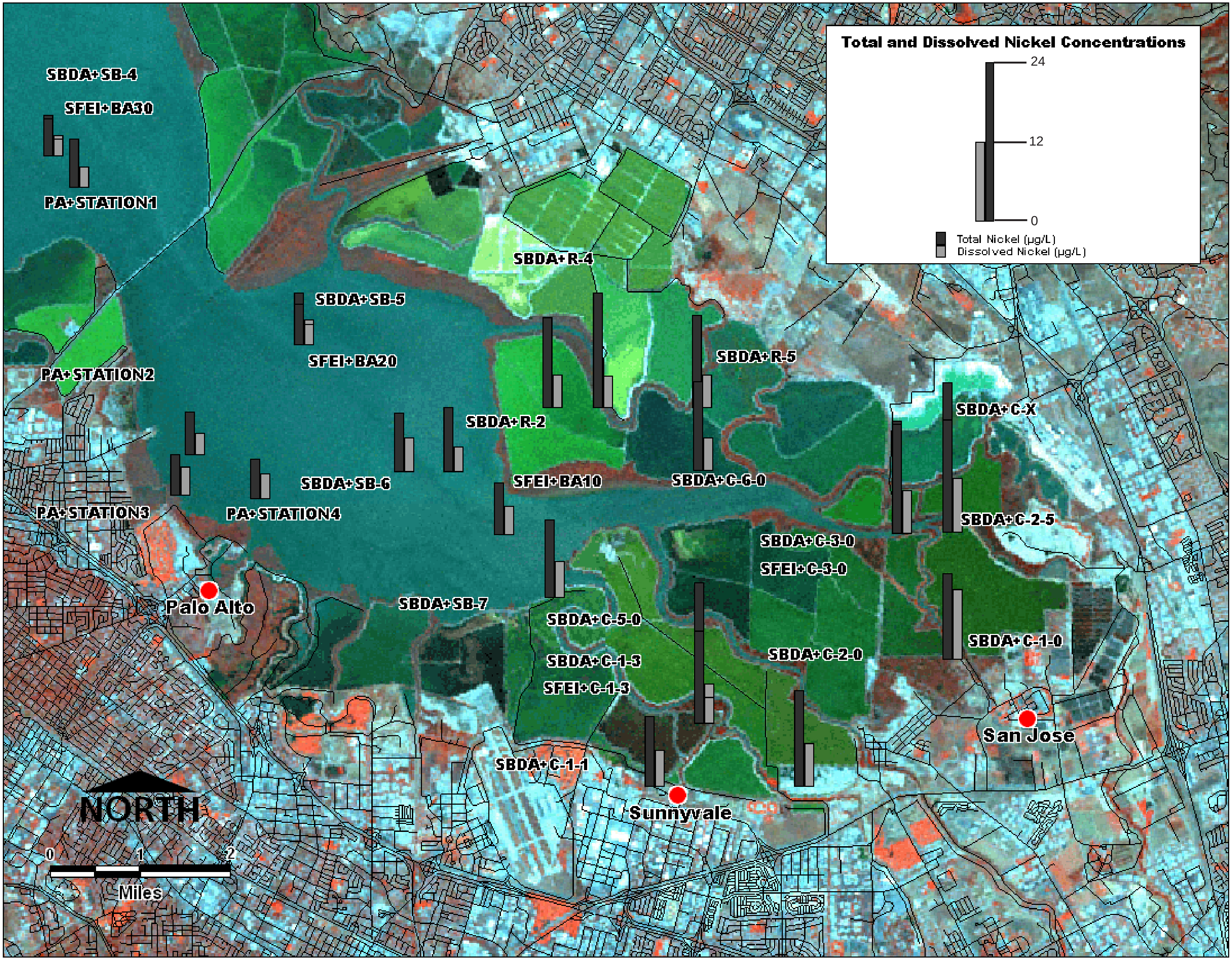


Figure 6-2b. Average total and dissolved nickel concentrations in water column at locations throughout Lower South San Francisco Bay.

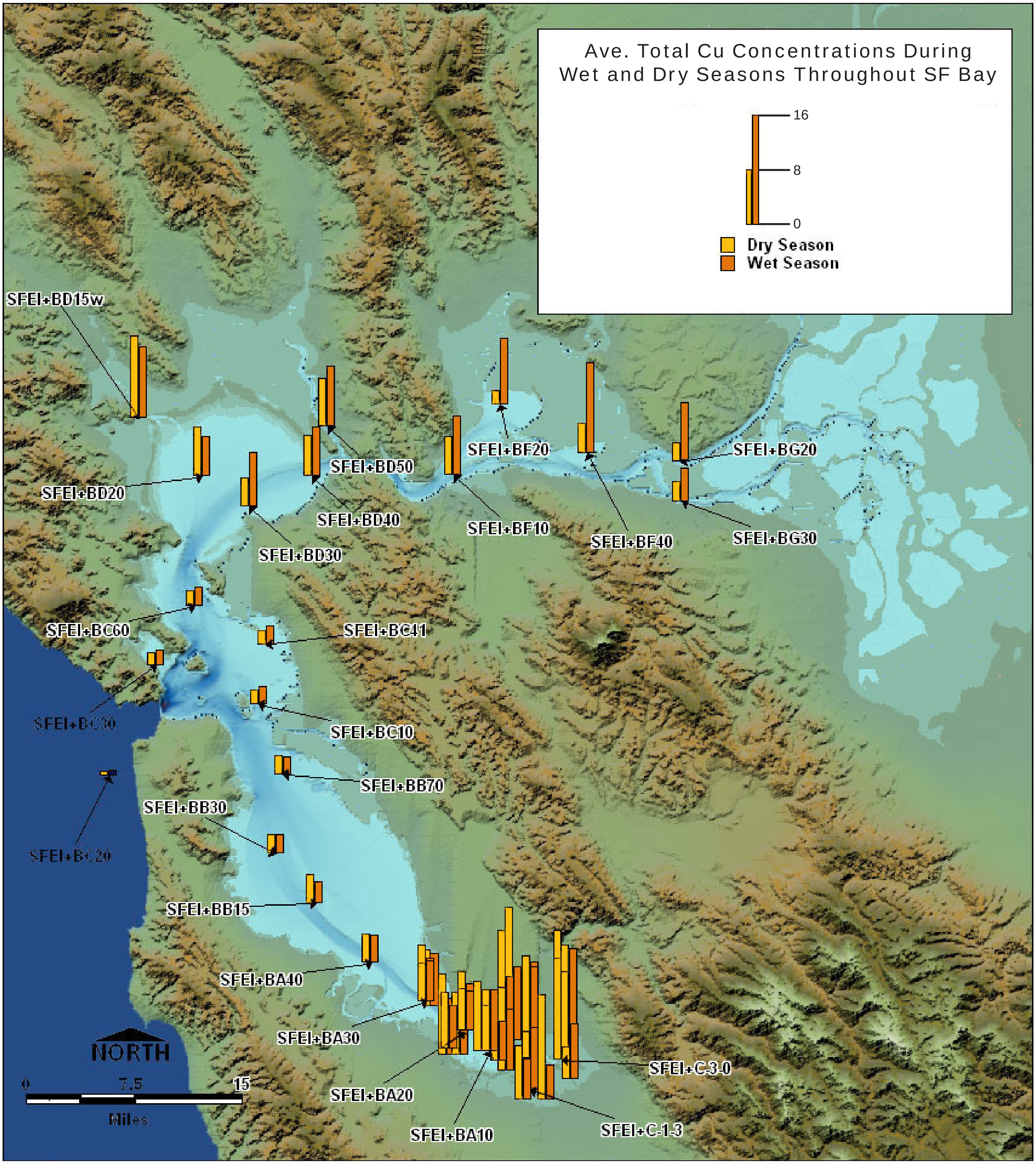


Figure 6-3a. Average total copper concentrations during dry and wet seasons at locations throughout San Francisco Bay.

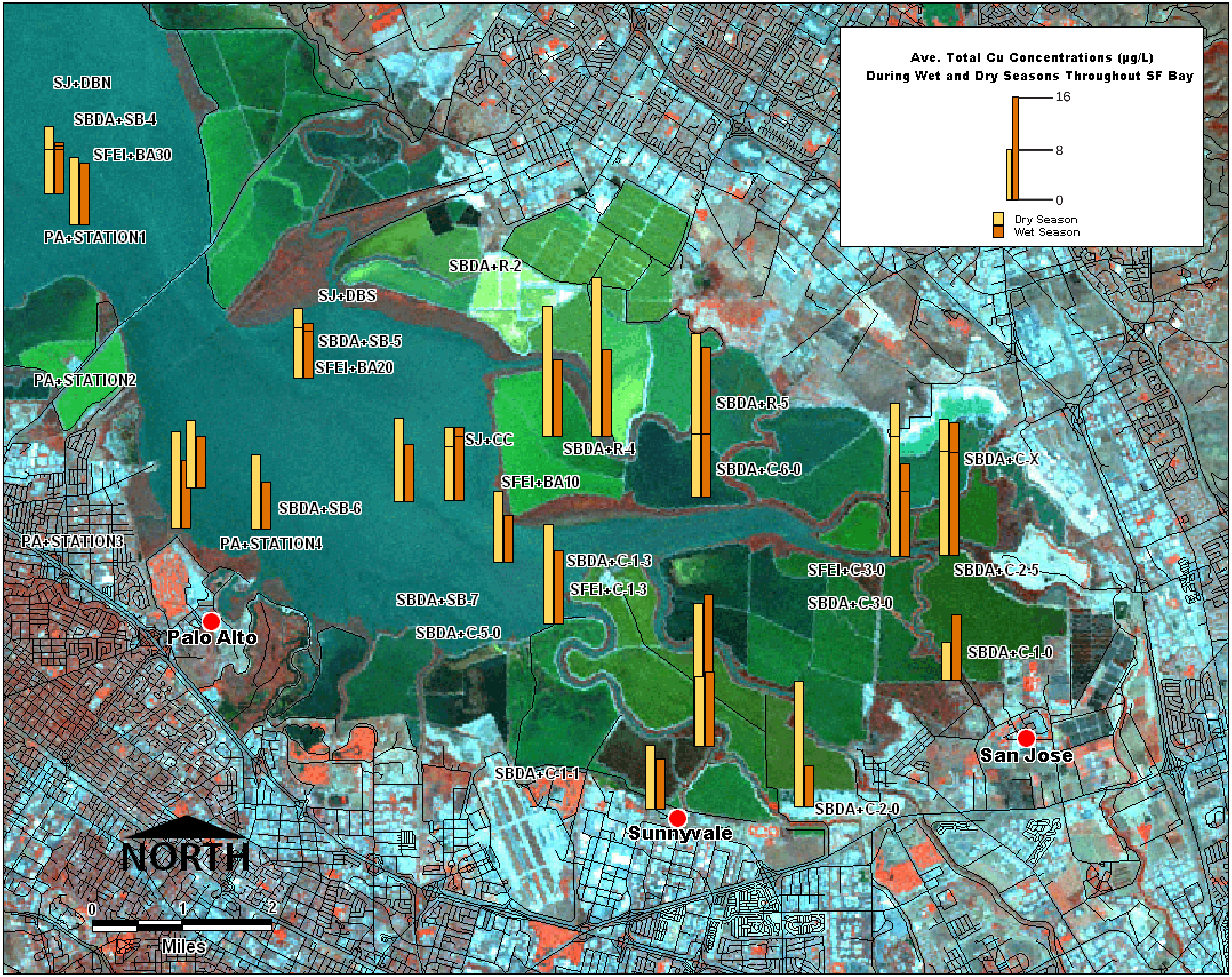


Figure 6-3b. Average total copper concentrations during dry and wet seasons at locations throughout Lower South San Francisco Bay.

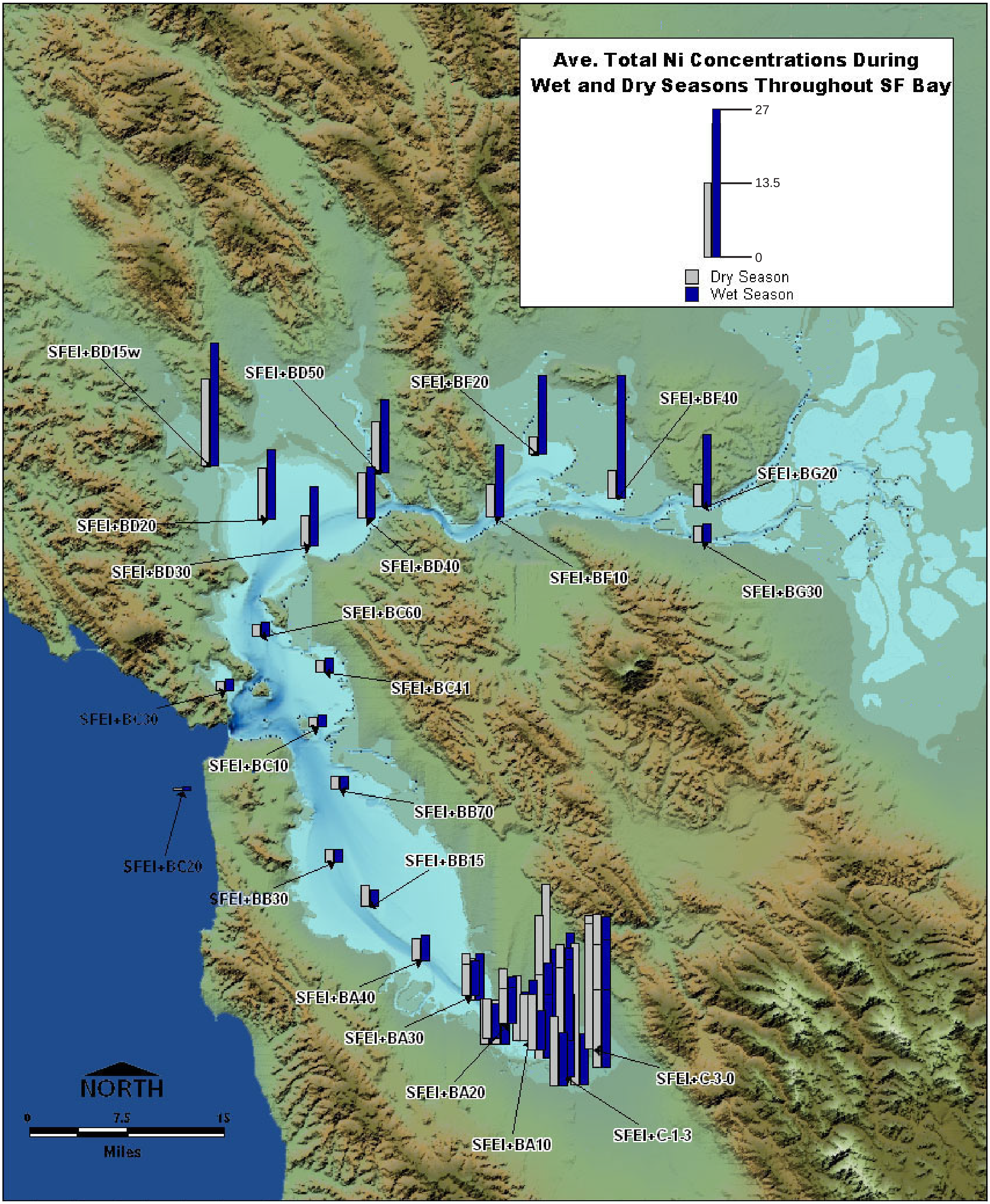


Figure 6-4a. Average total nickel concentrations during dry and wet seasons at locations throughout San Francisco Bay.

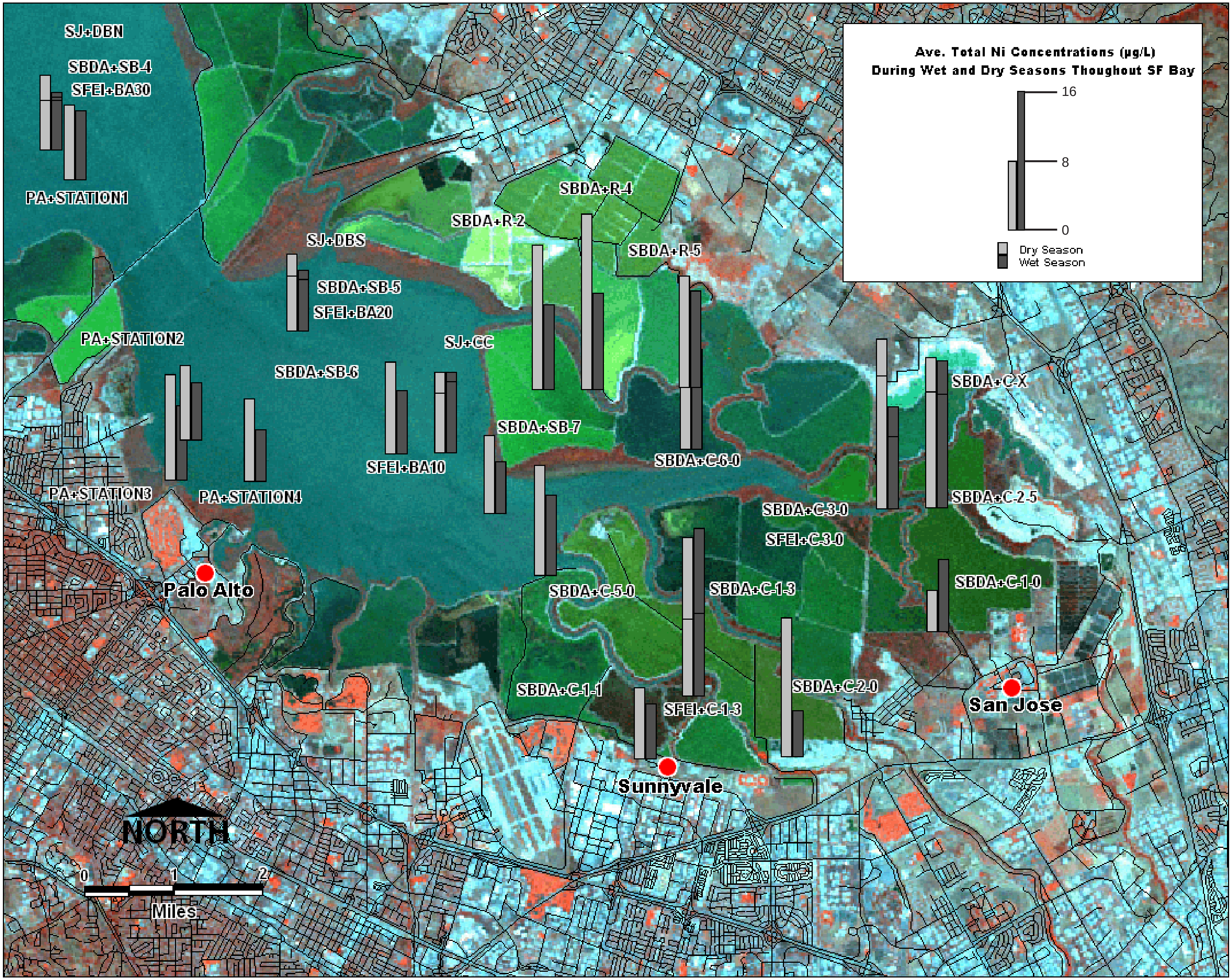


Figure 6-4b. Average total nickel concentrations during dry and wet seasons at locations throughout Lower South San Francisco Bay.

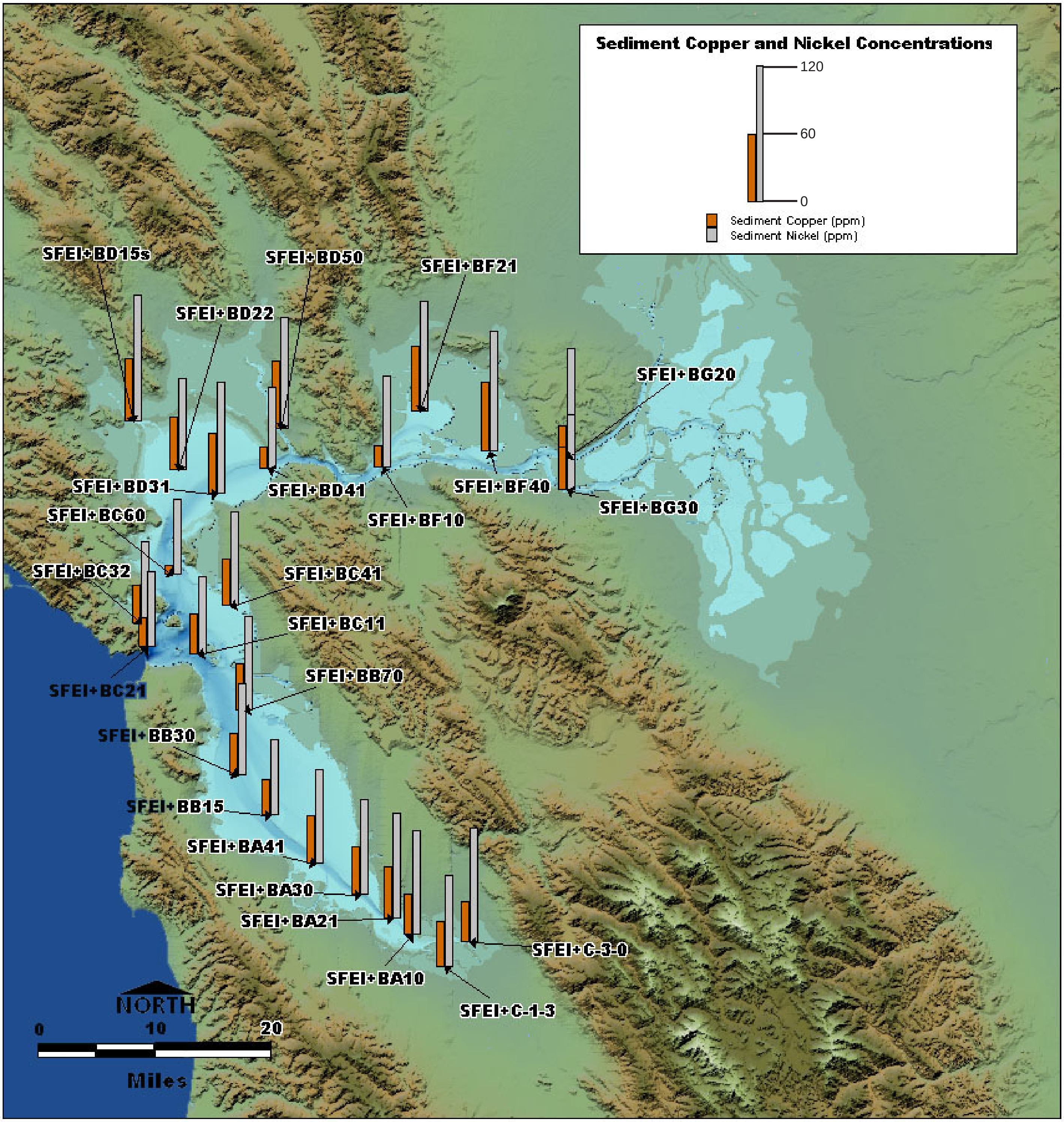
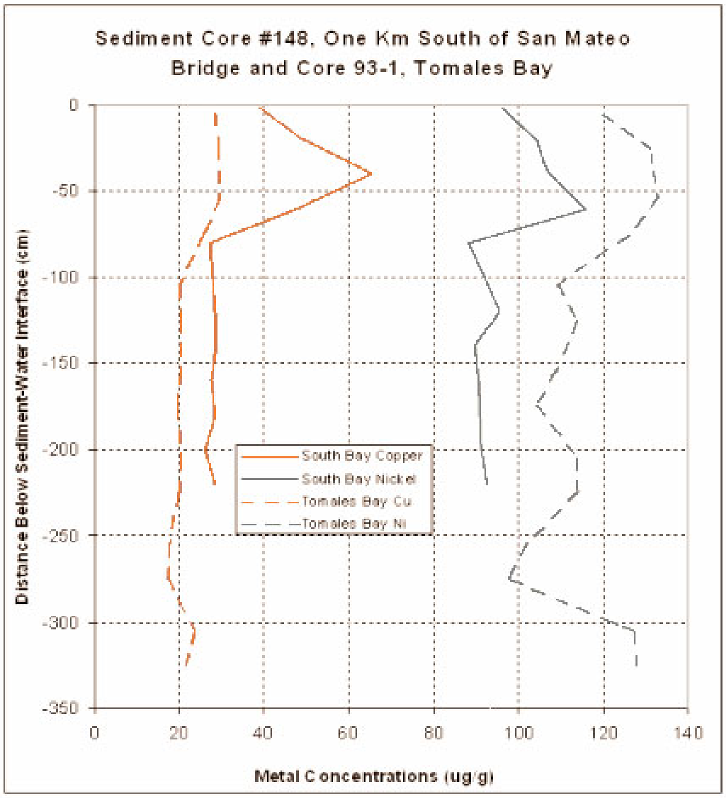


Figure 6-5a. Surficial sediment copper and nickel concentrations at locations throughout San Francisco Bay, and selected results from core samples.



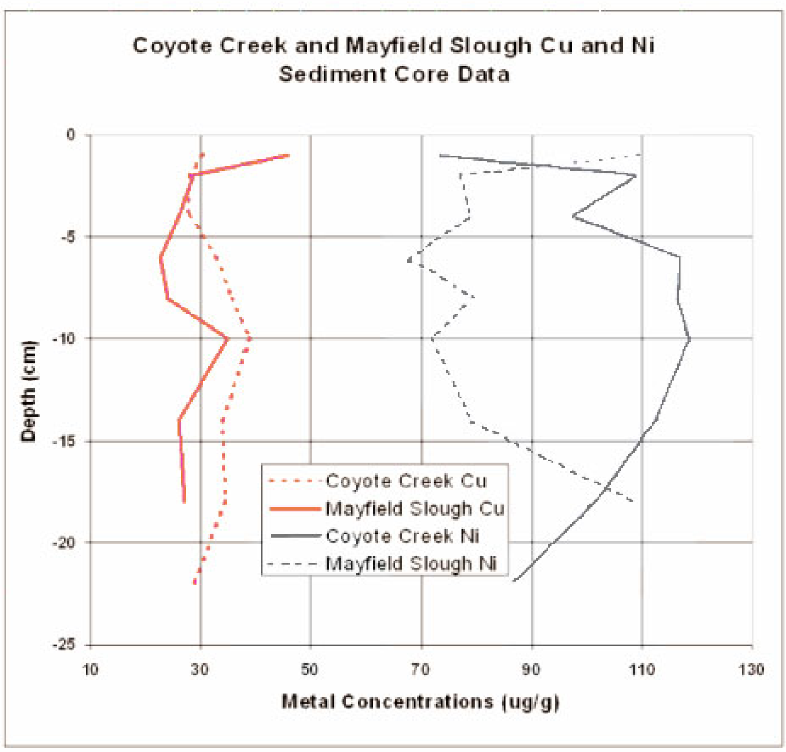


Figure 6-5b. Copper and nickel concentrations in sediments taken from South Bay, Lower South Bay, and Tomales Bay (background).

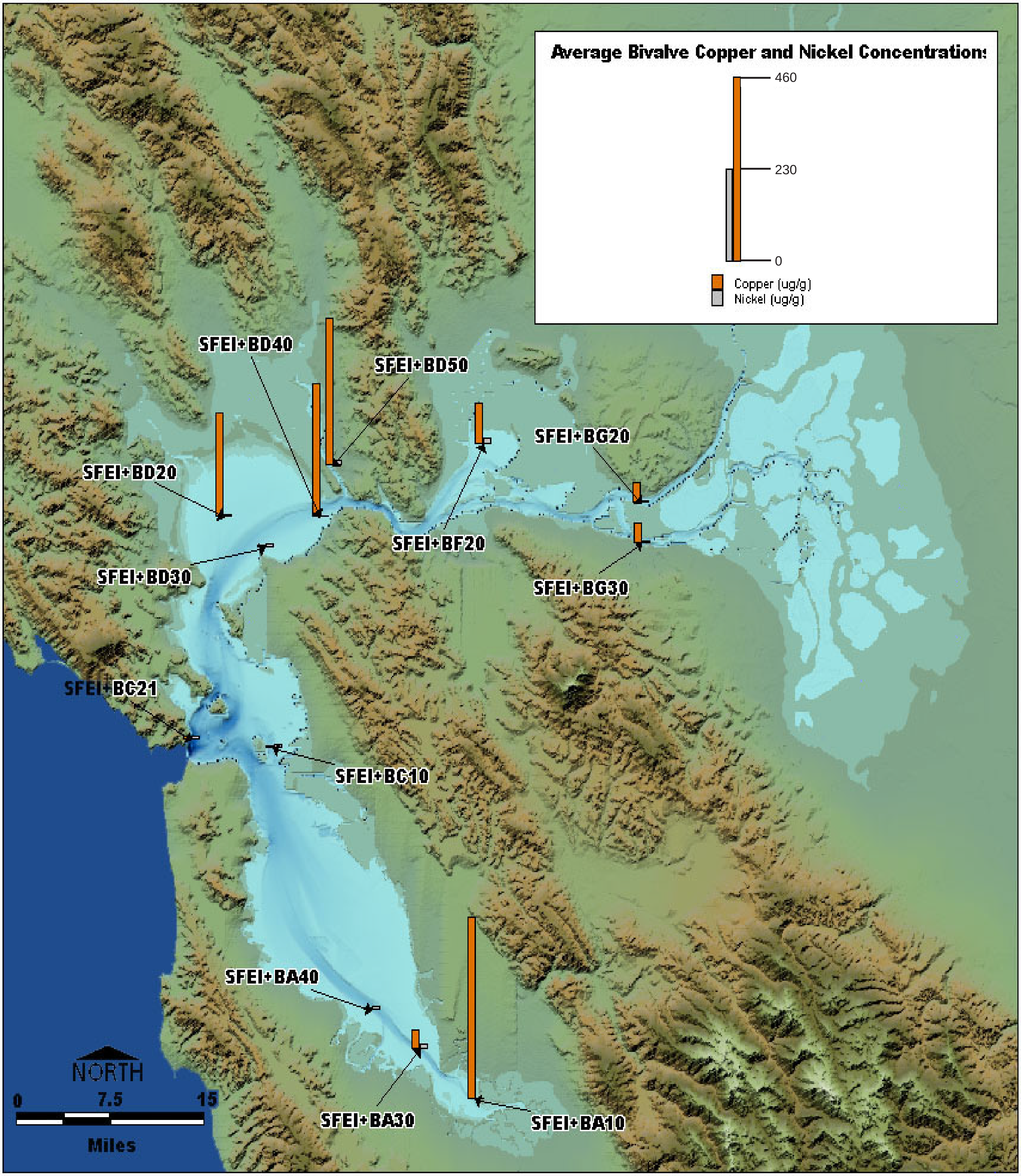


Figure 6-6. Average concentrations of copper and nickel in translocated bivalves at locations throughout San Francisco Bay.

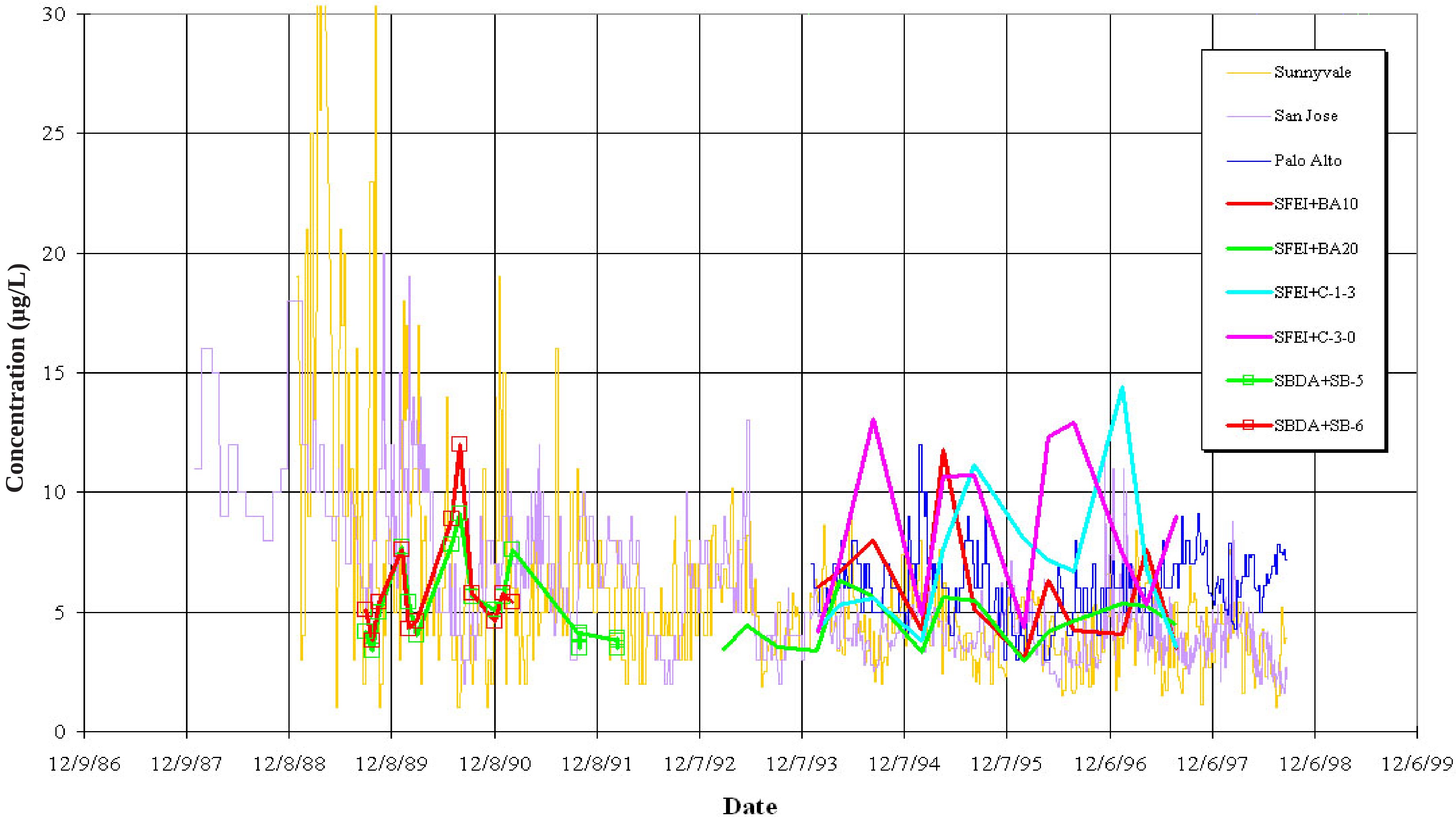


Figure 6-7a. Total copper concentrations in effluent of three Lower South San Francisco Bay WastewaterTreatment Plants compared with total copper concentrations at locations in Lower South San Francisco Bay.

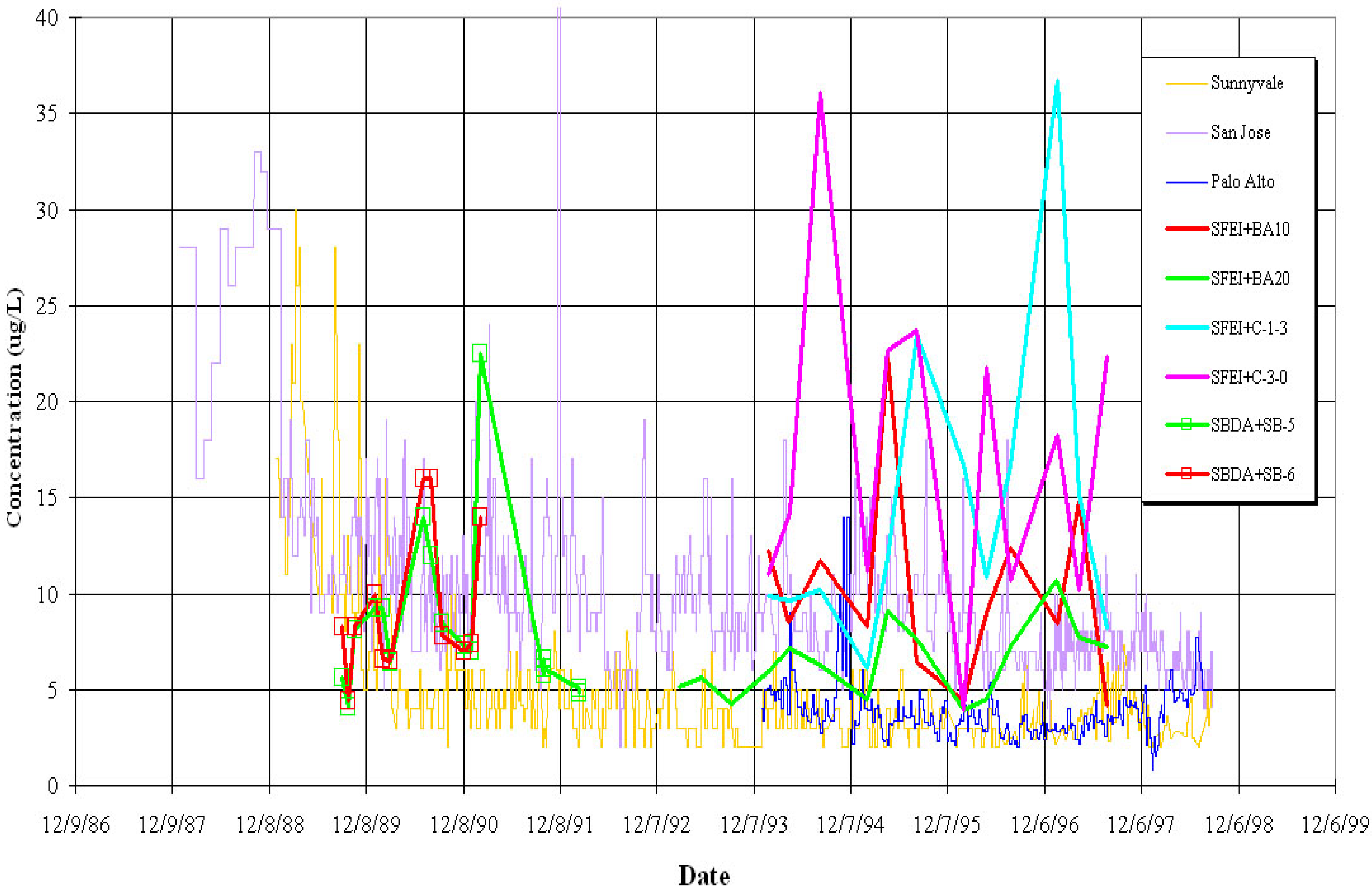


Figure 6-7b. Total nickel concentrations in effluent of three Lower South San Francisco Bay WastewaterTreatment Plants compared with total nickel concentrations at locations in Lower South San Francisco Bay.

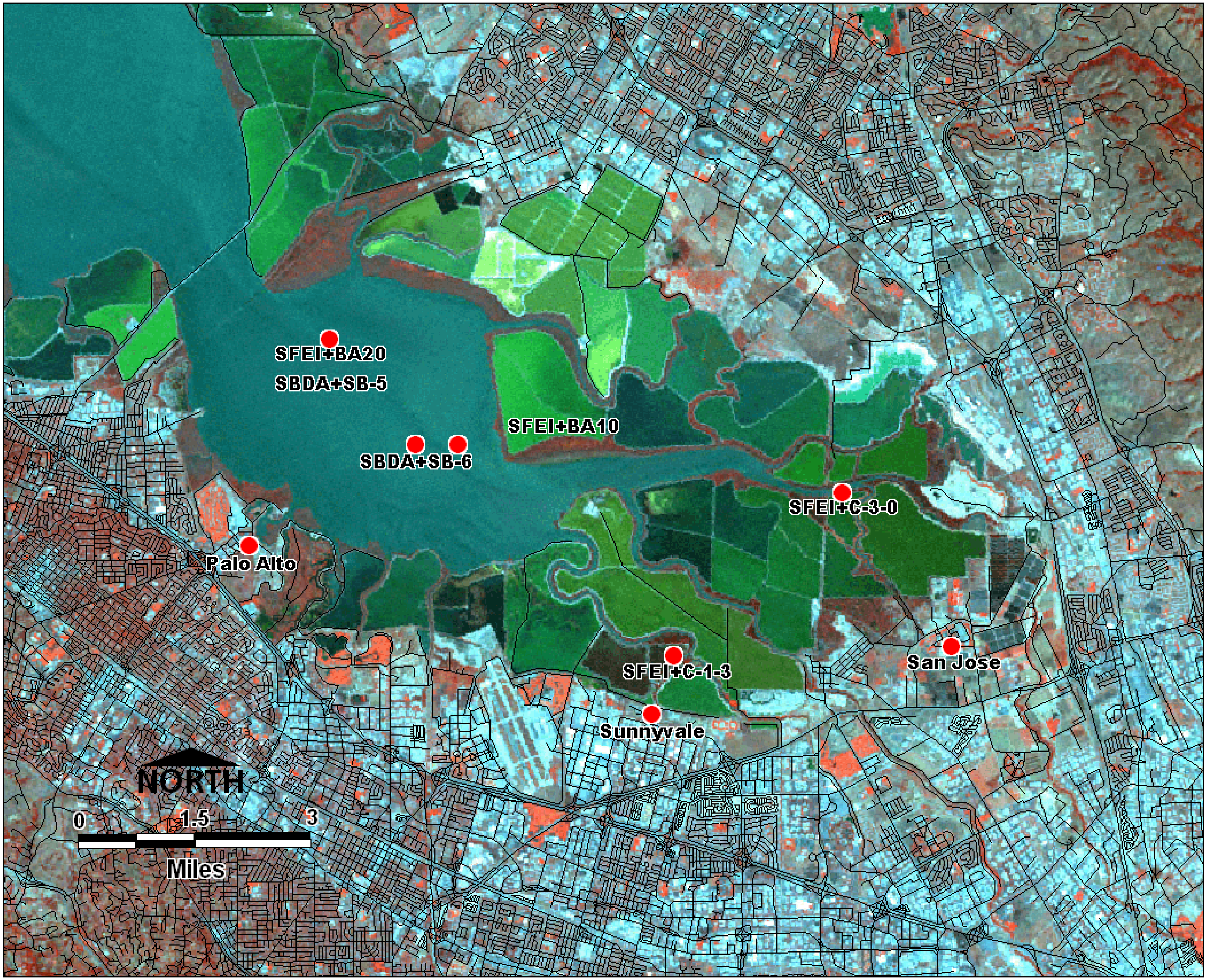


Figure 6-7c.   Location of sampling stations and three wastewater treatment plants in Lower South San Francisco Bay.

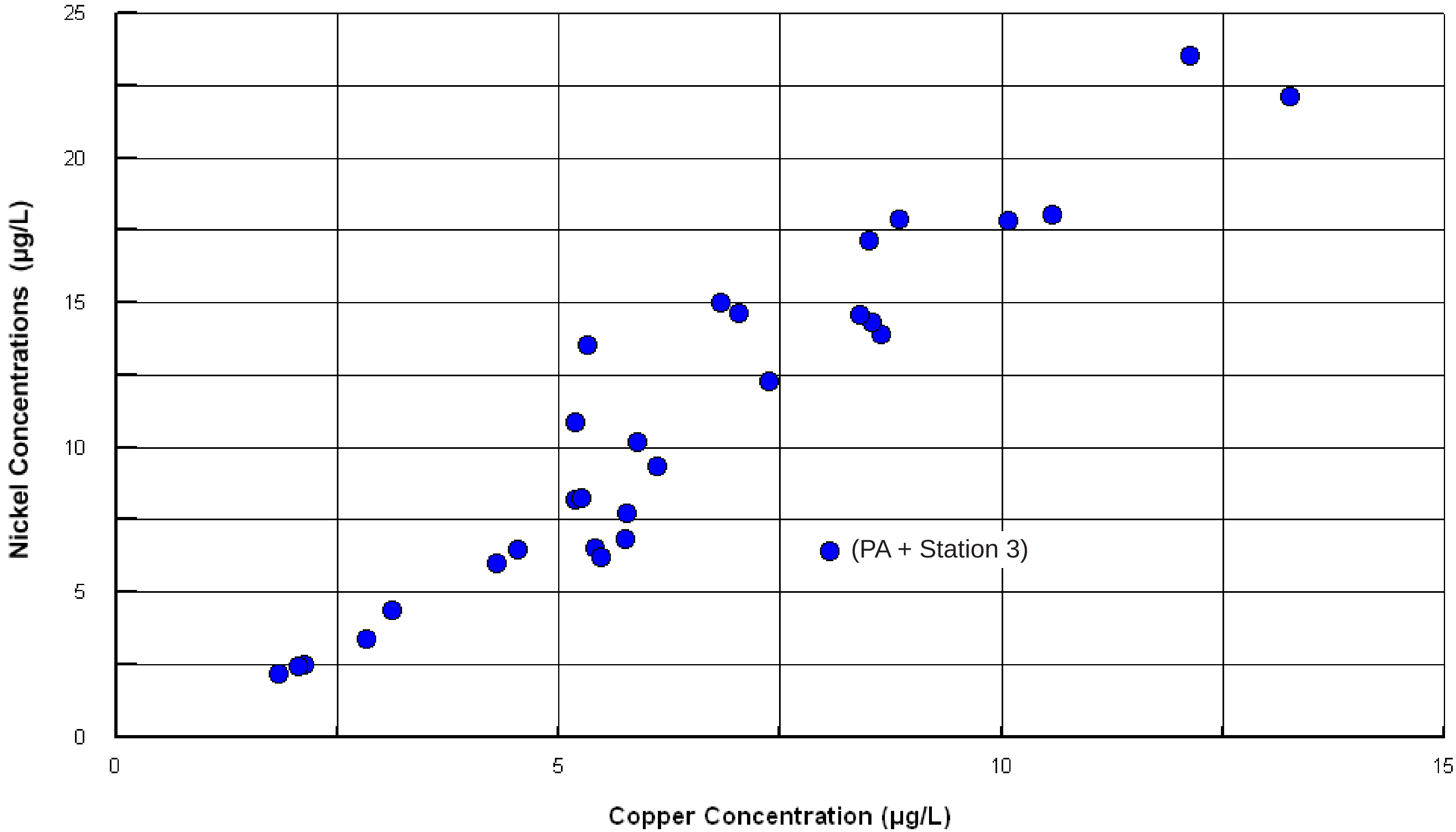


Figure 6-8. Correlation between average total nickel and total copper concentrations at locations in South San Francisco Bay.

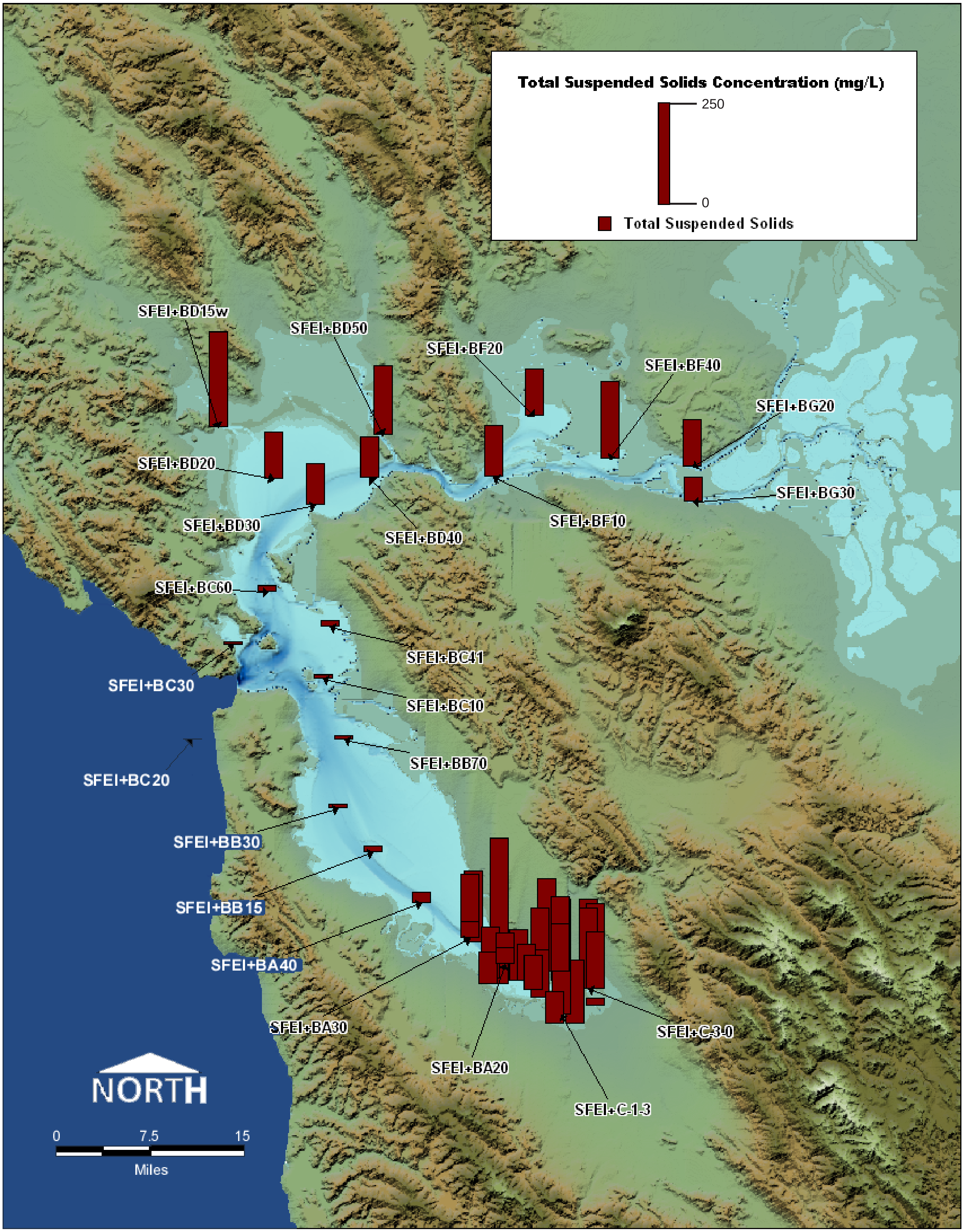


Figure 6-9a. Average total suspended solids concentration at locations throughout San Francisco Bay.

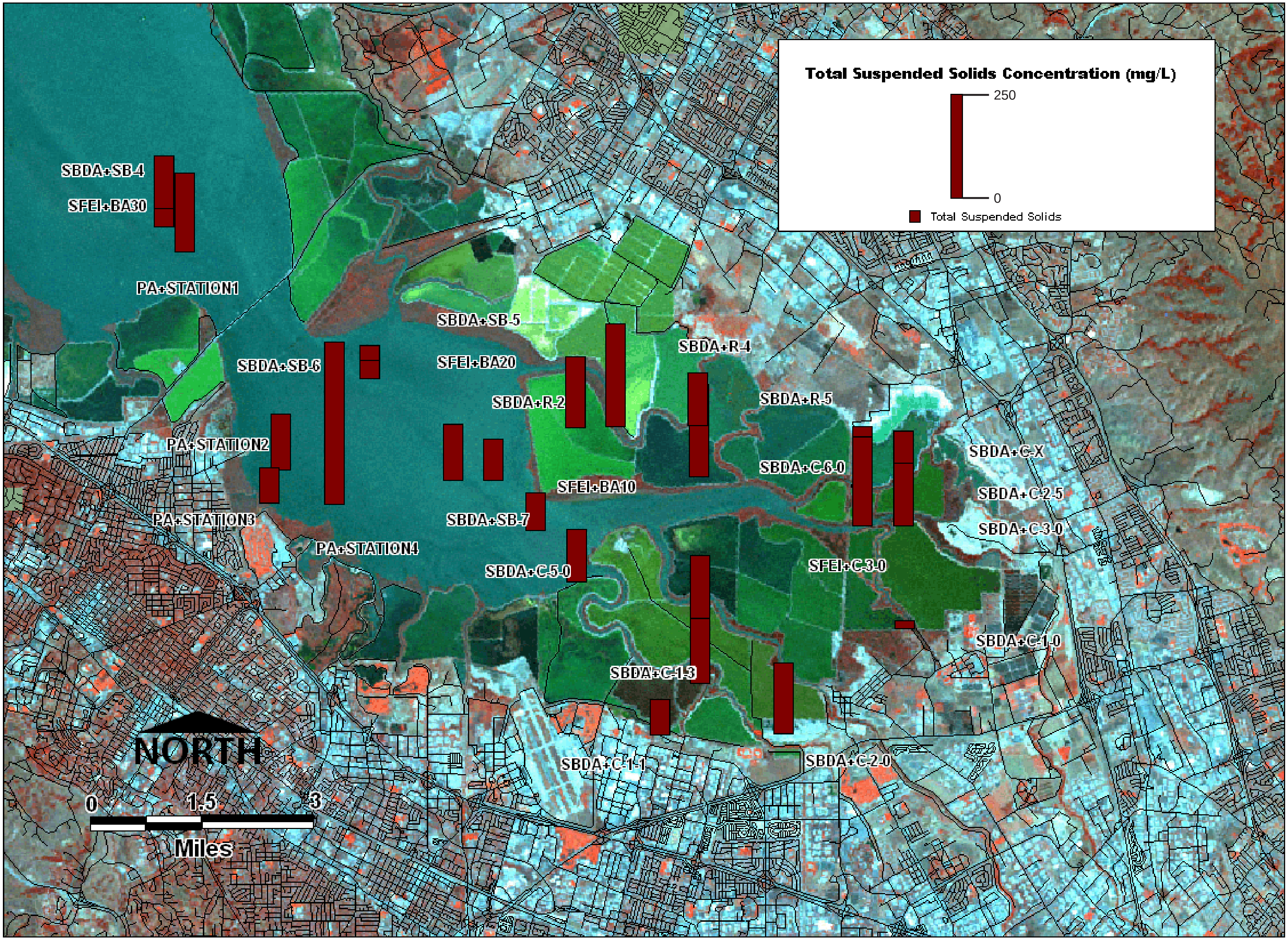


Figure 6-9b. Average suspended solids concentrations at locations throughout Lower South San Francisco Bay.

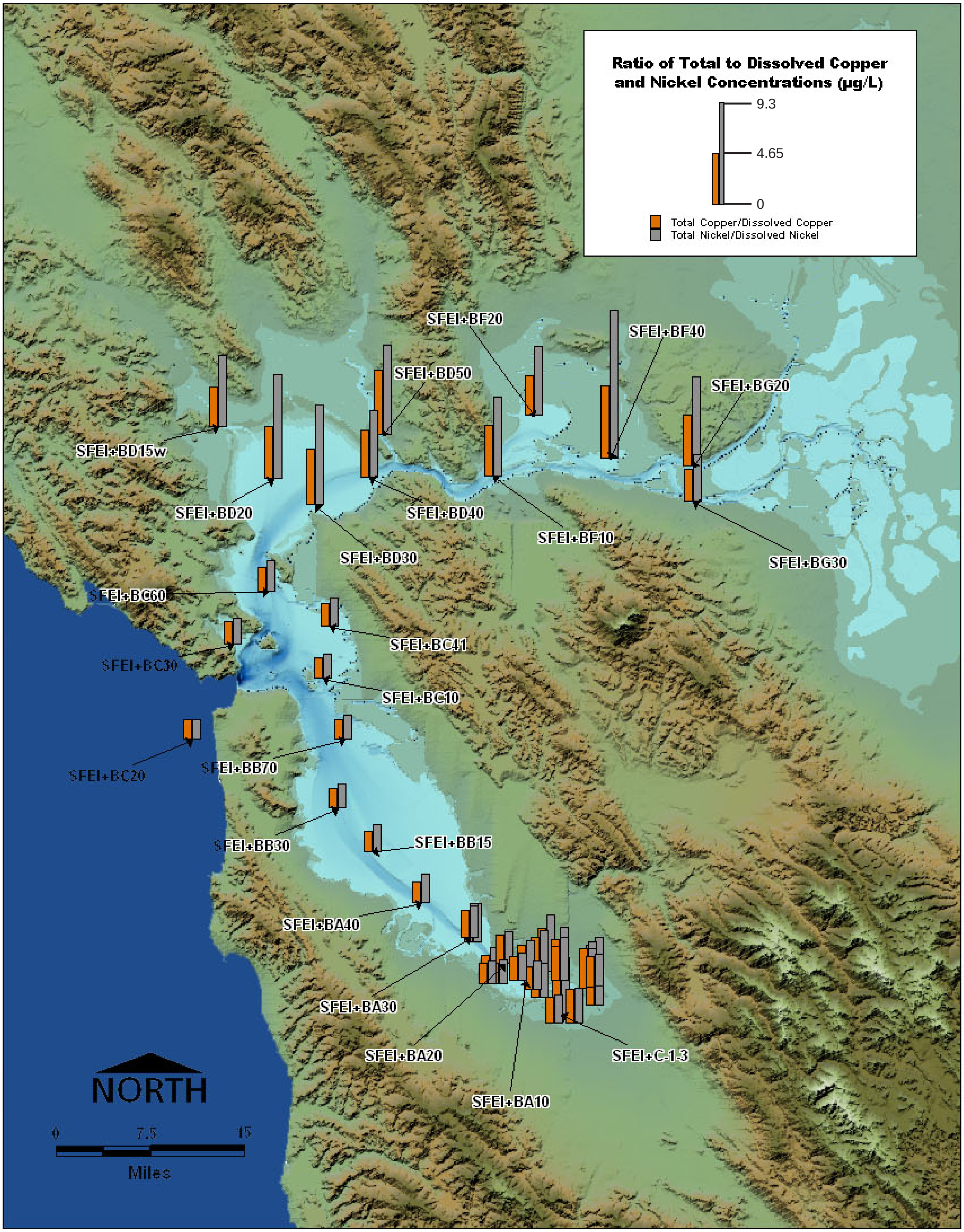


Figure 6-9c. Ratio of total to dissolved copper and nickel concentrations at locations throughout San Francisco Bay.

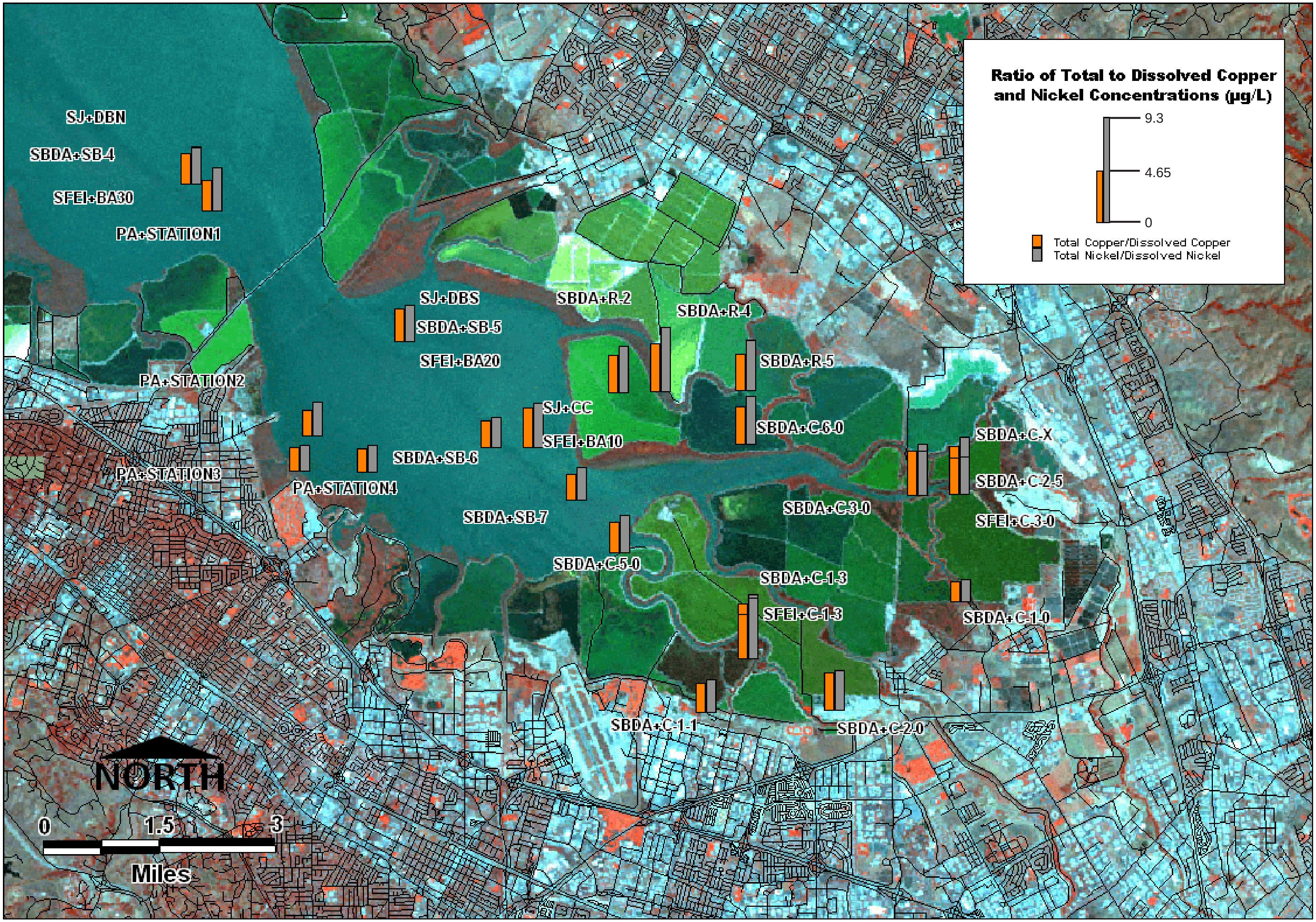


Figure 6-9d. Ratio of total to dissolved copper and nickel concentrations at locations throughout Lower South San Francisco Bay.

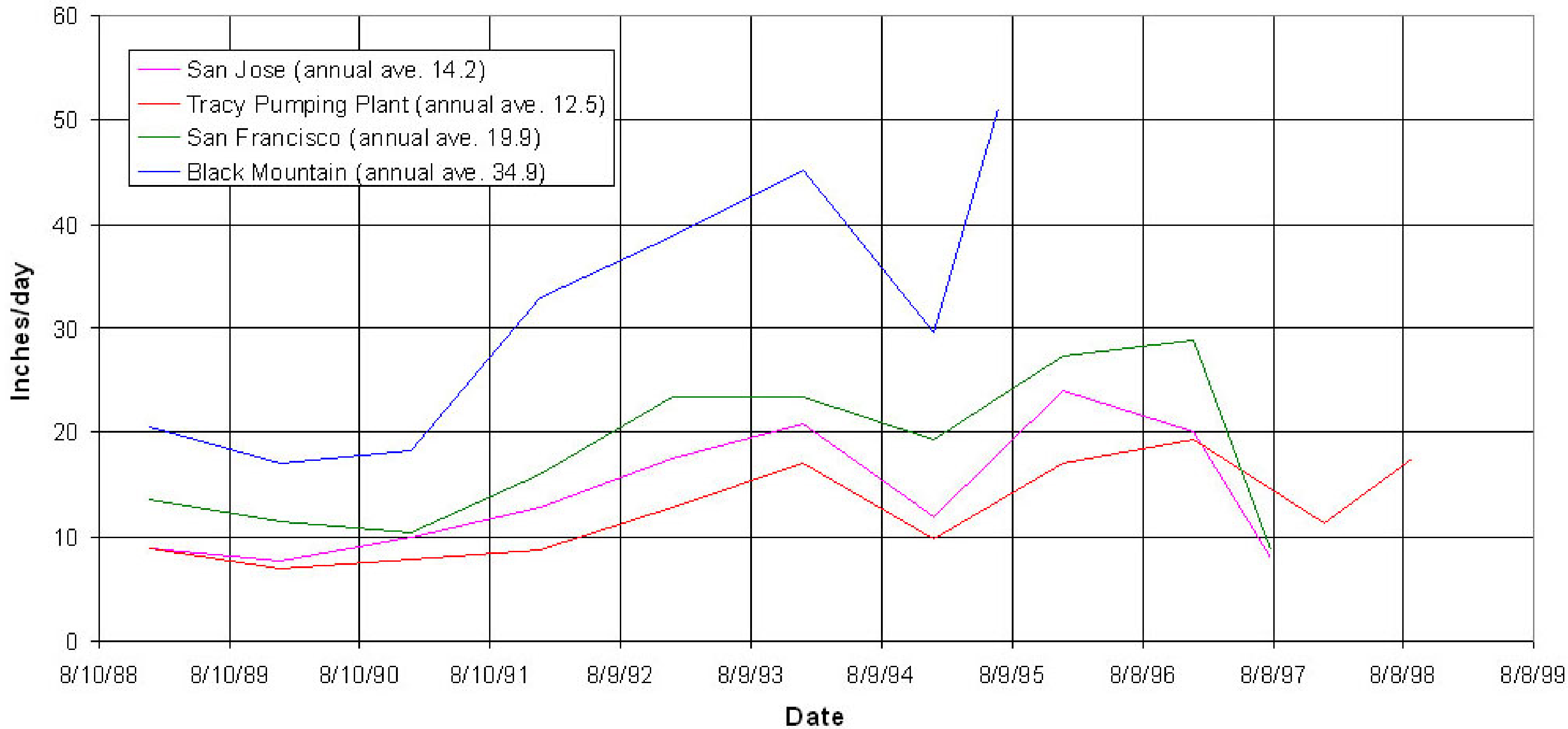


Figure 6-10a. Annual precipitation at San Jose, San Francisco, Tracy Pumping Plant, and Black Mountain.

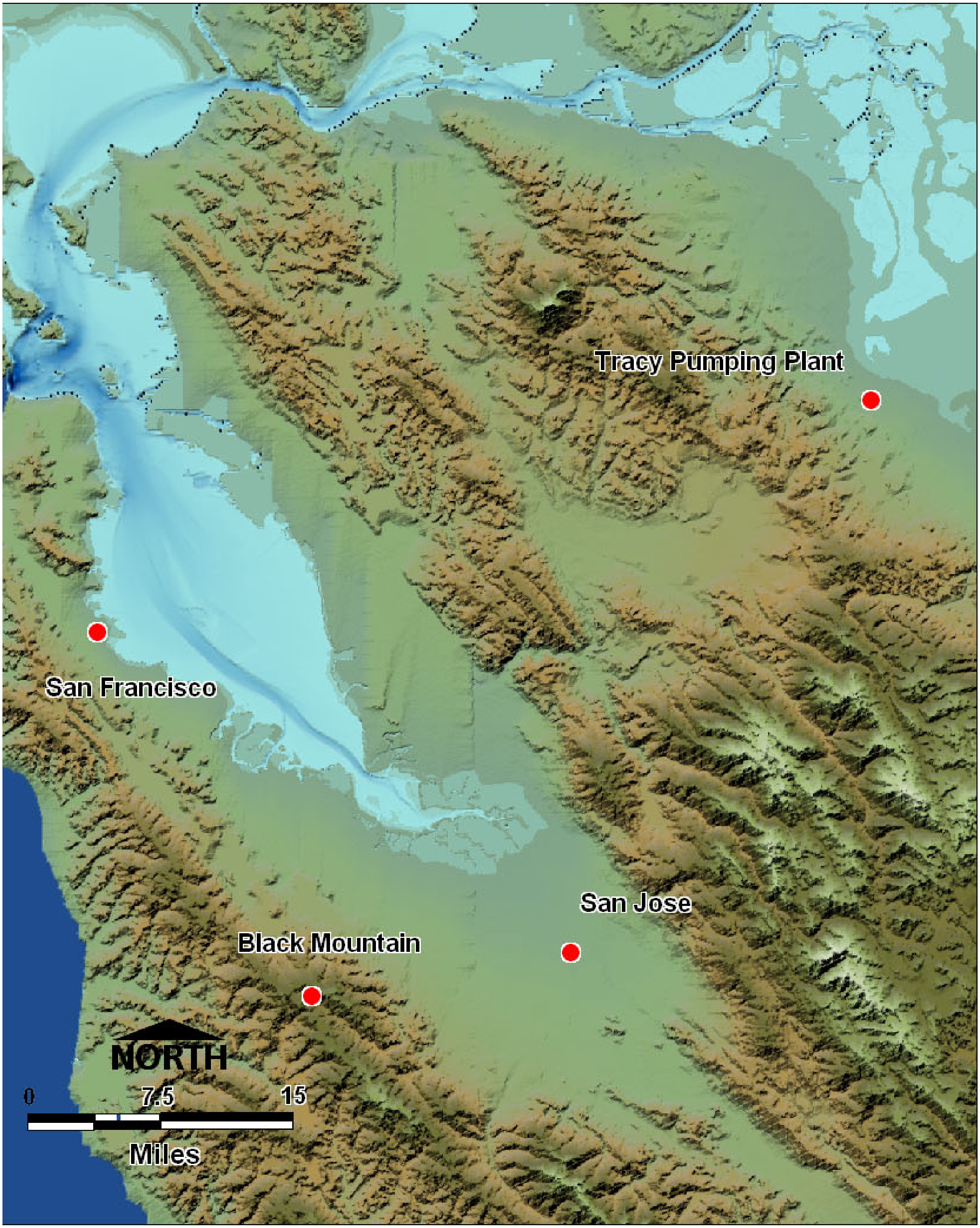


Figure 6-10b. Locations of four stations where precipitation is reported.

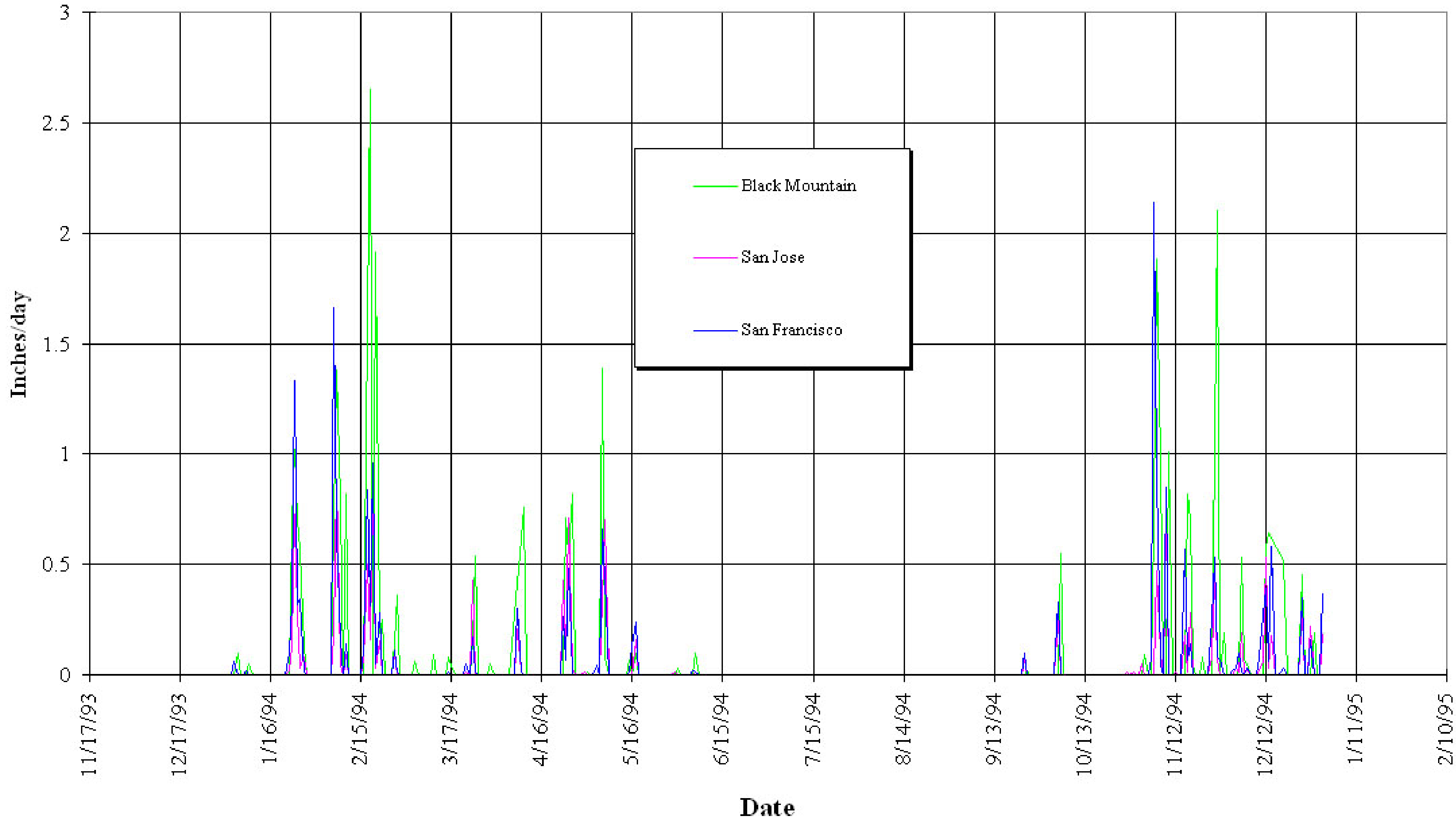


Figure 6-10c. Daily precipitation over one-year period at four locations in San Francisco Bay area.

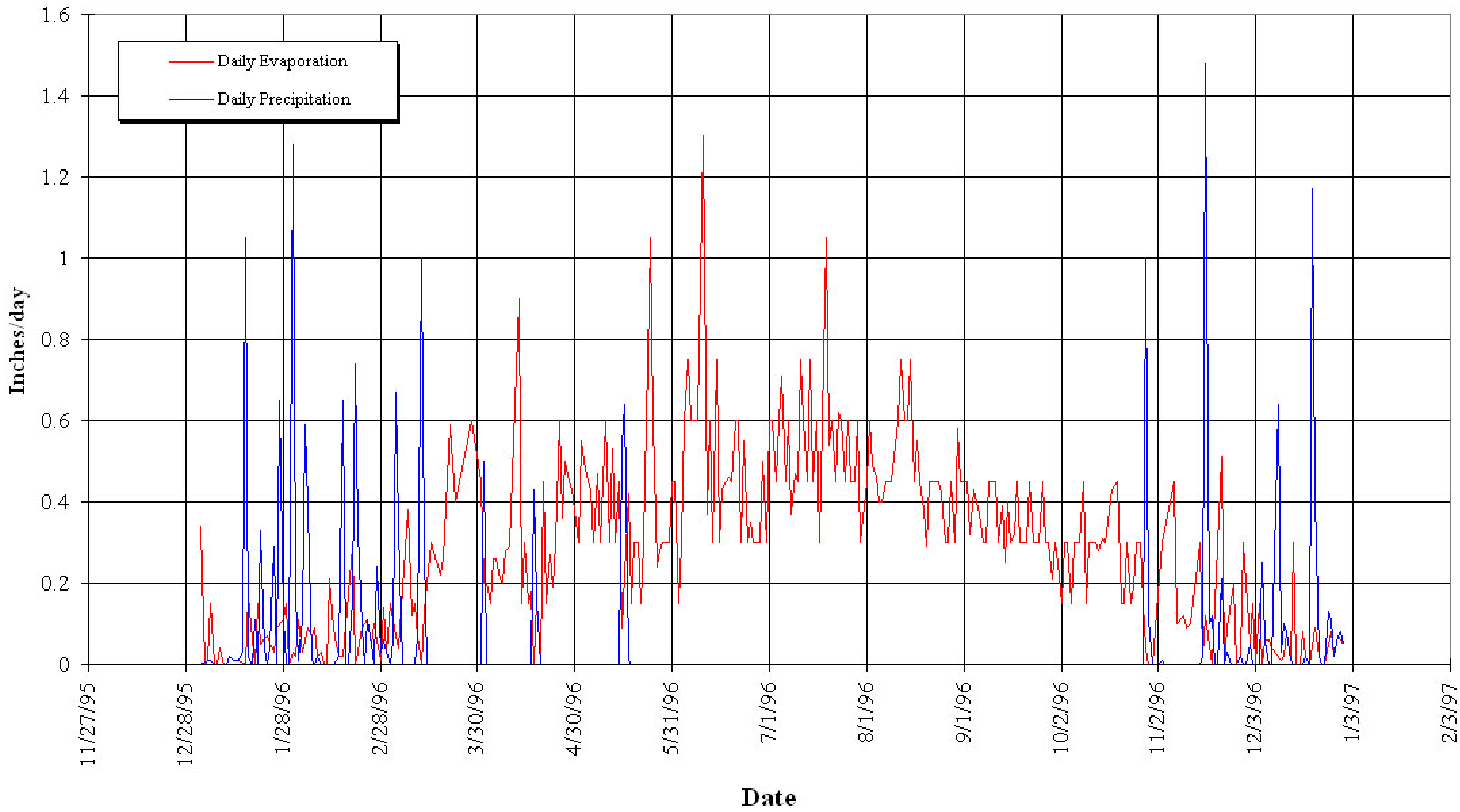


Figure 6-11. Precipitation and evaporation for one year (1996-1997) at the Tracy Pumping Station.

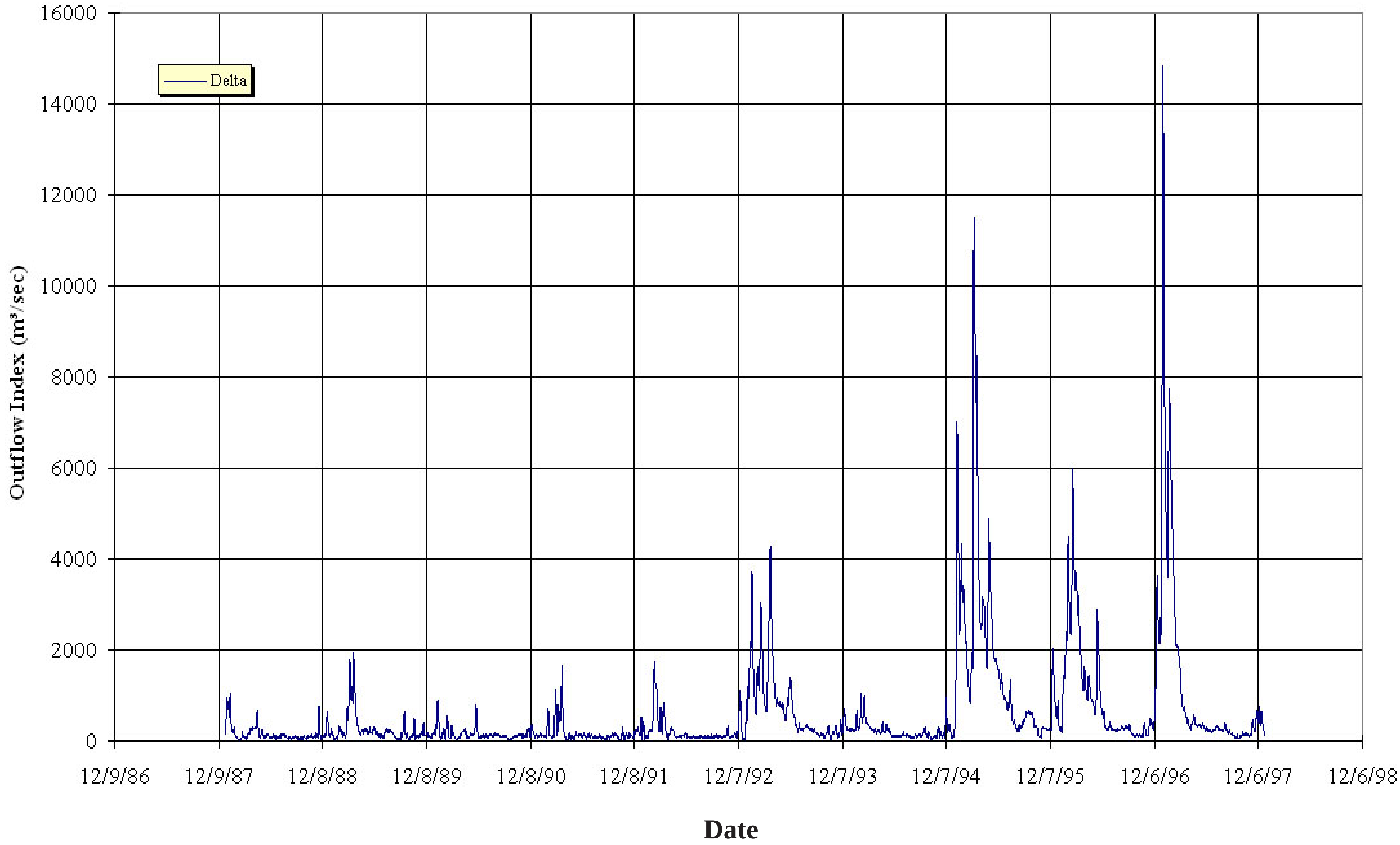


Figure 6-12a. Time series of Delta inflow rate and streamflows from Lower San Francisco Bay from 1987-1997.

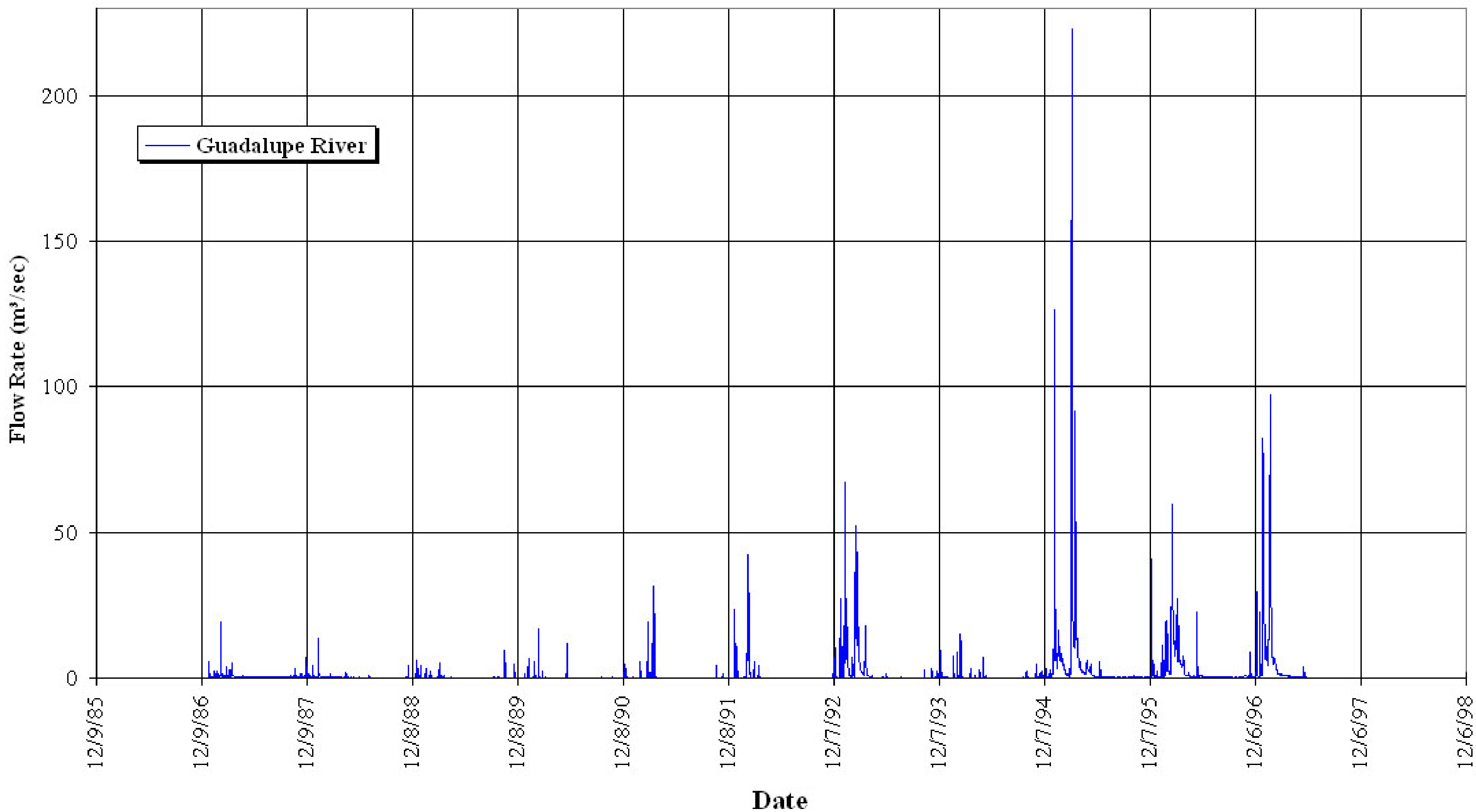


Figure 6-12b. Guadalupe River discharge from 1986-1996.

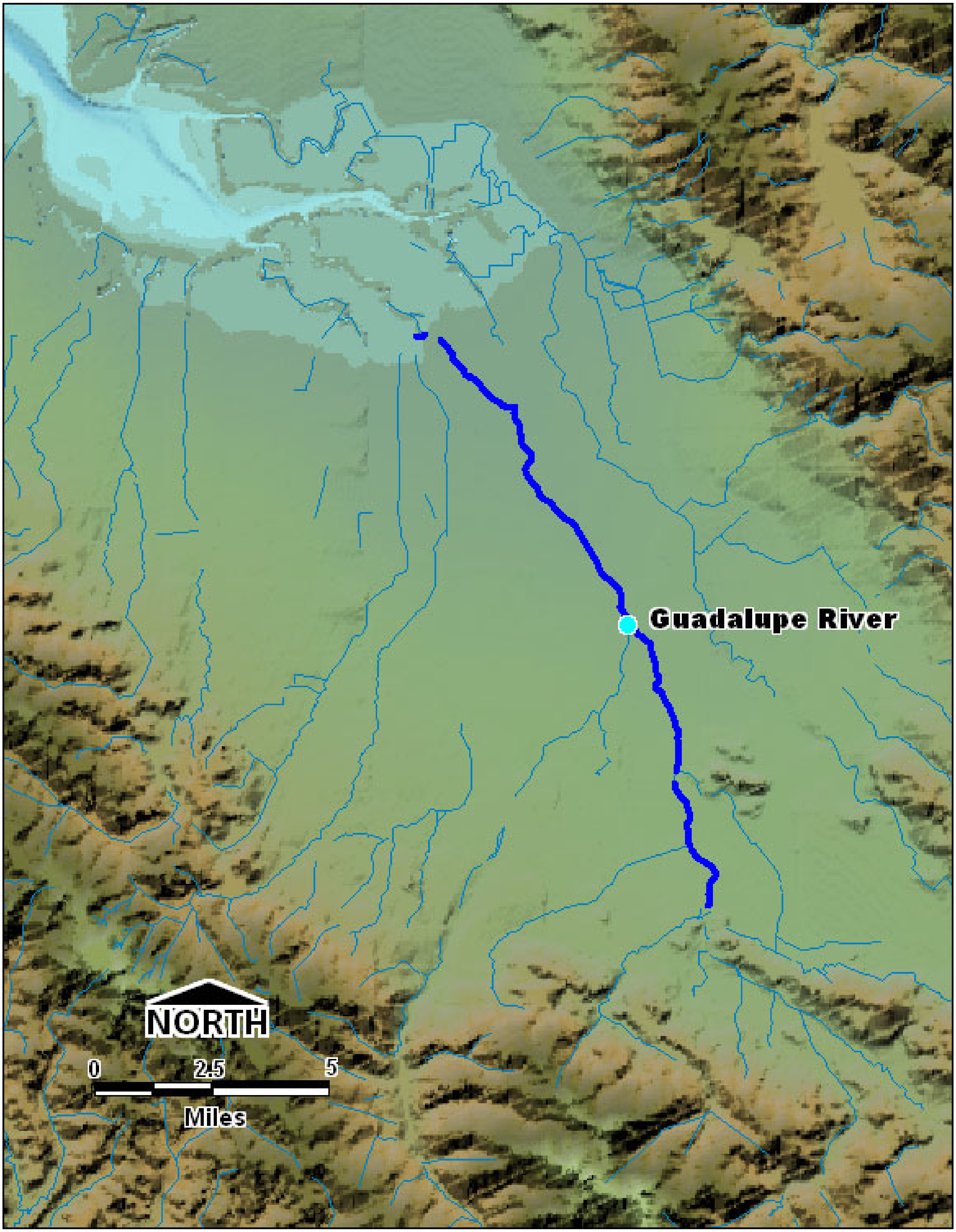


Figure 6-12c. Location of Guadalupe River Gaging Station.

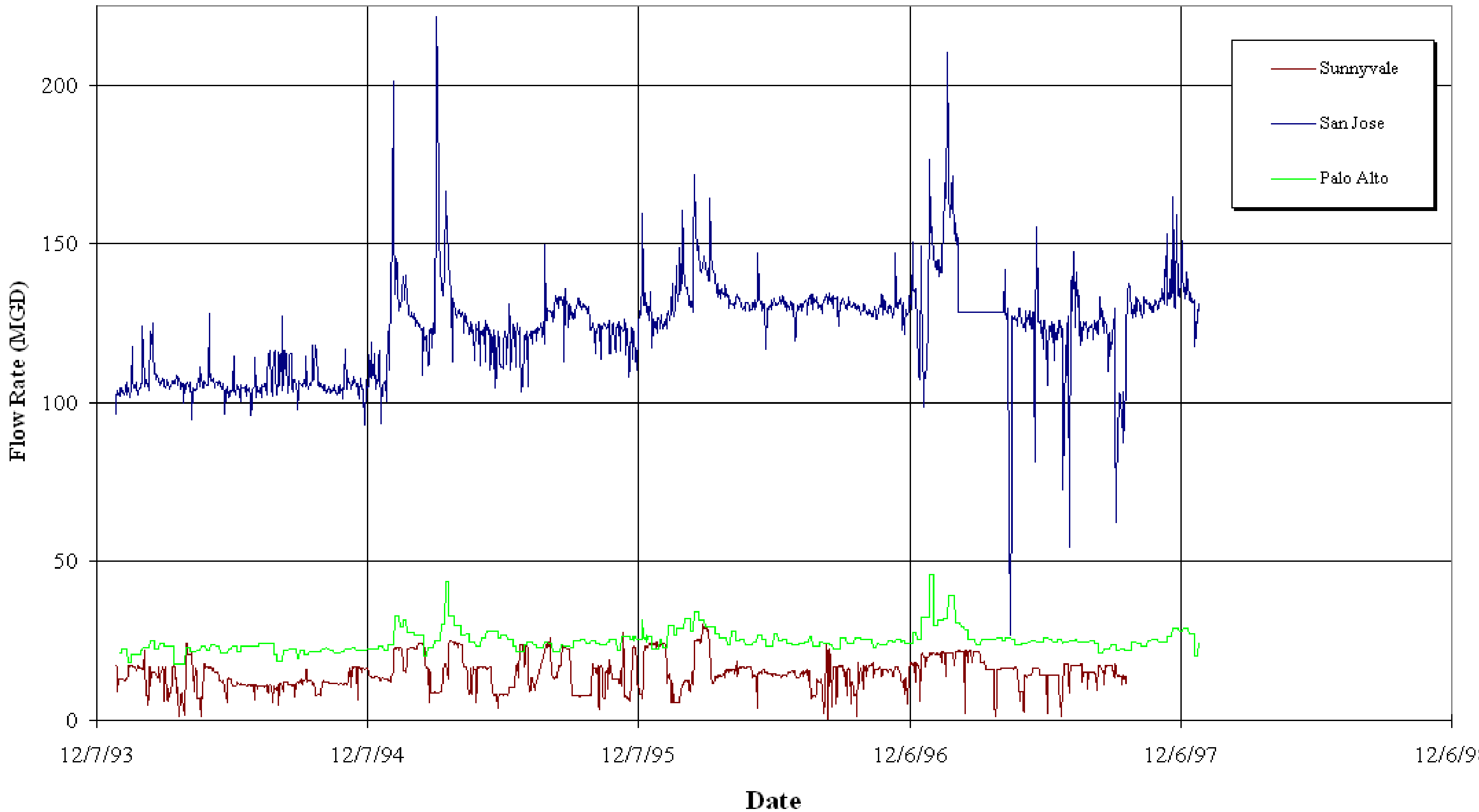


Figure 6-13. Comparison of fresh water volumetric discharges from point sources into Lower South San Francisco Bay.

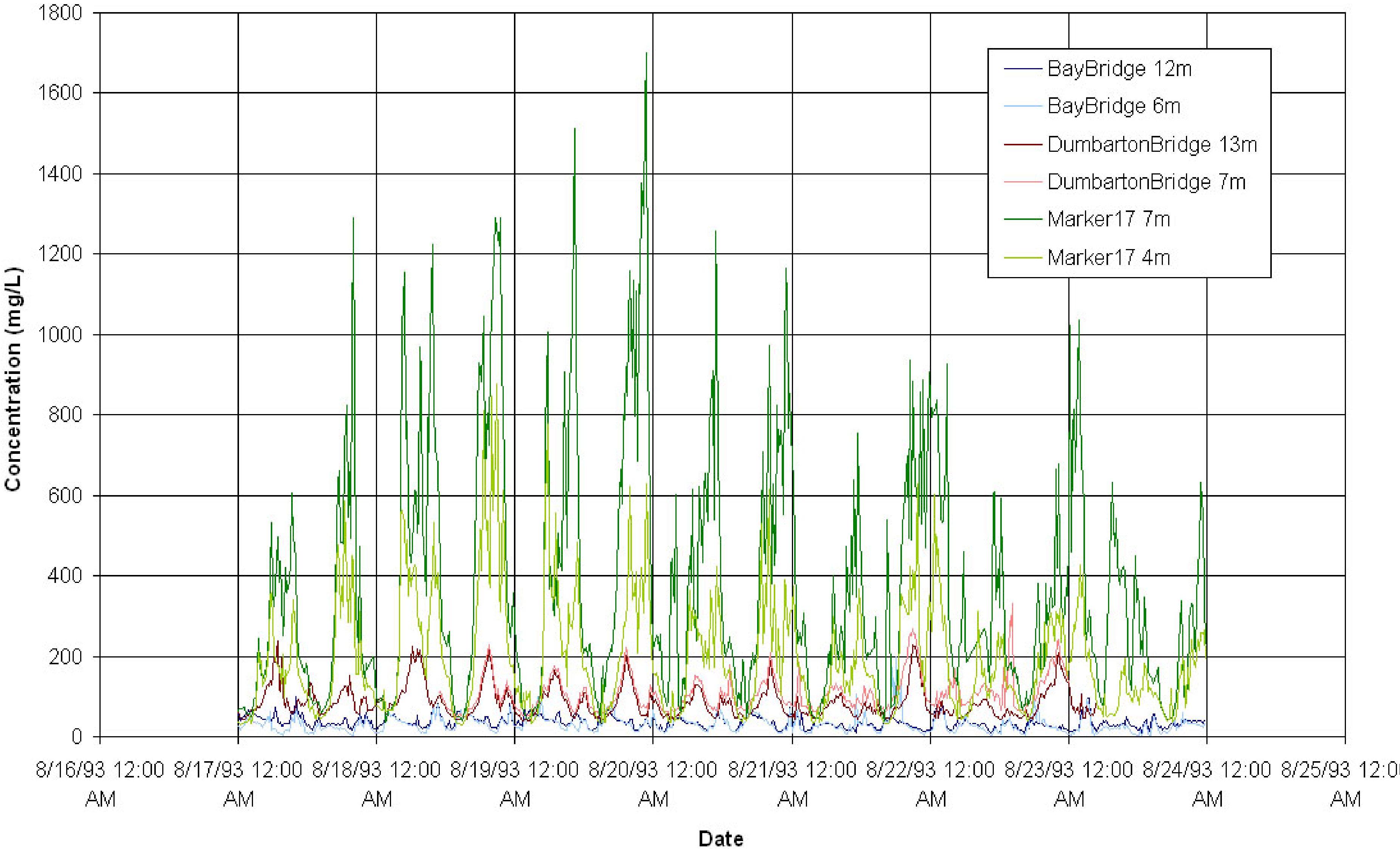


Figure 6-14. Total suspended solids concentrations in San Francisco Bay at three locations over a one-week period.

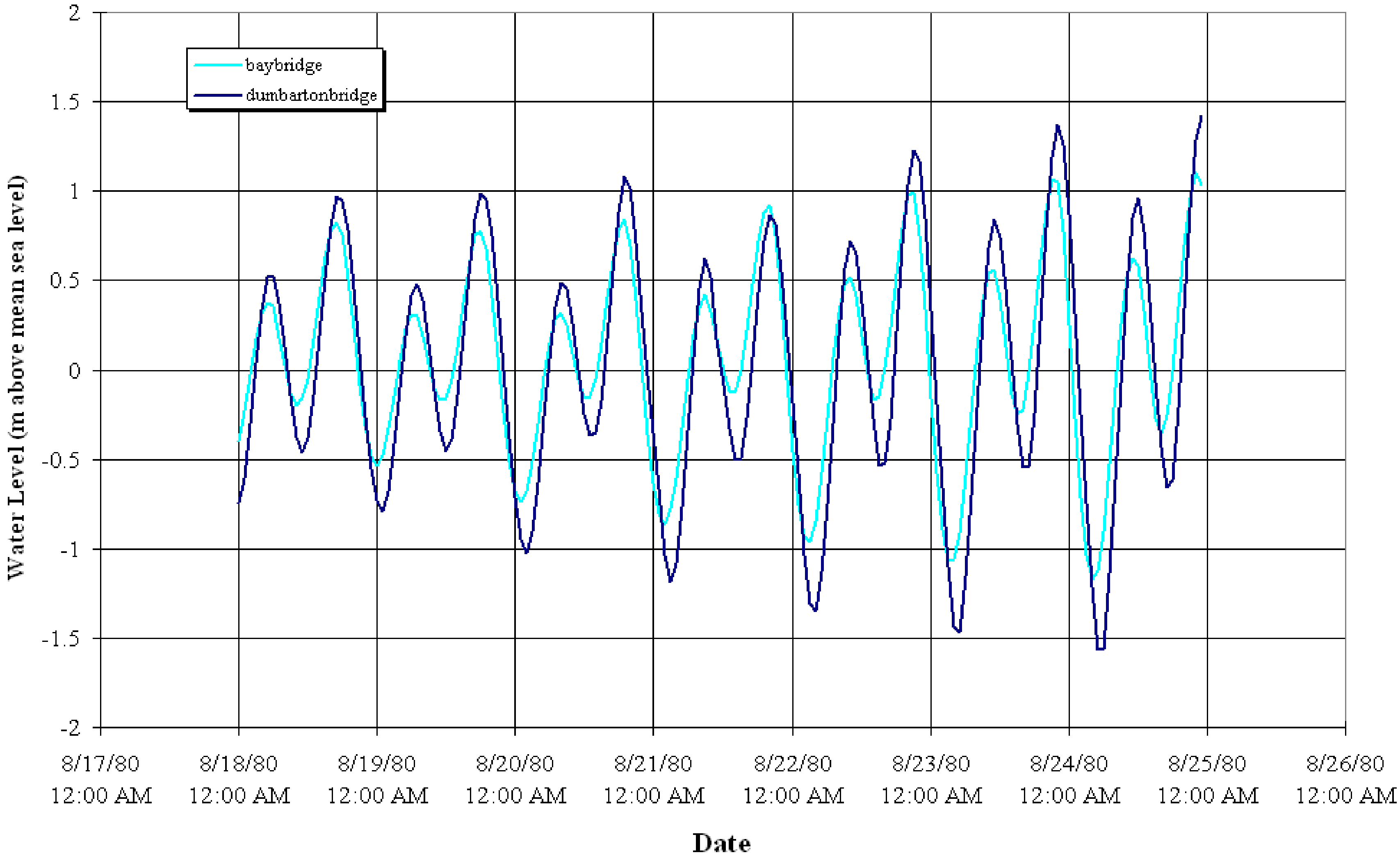


Figure 6-15. Tidal elevations at two locations in South San Francisco Bay.

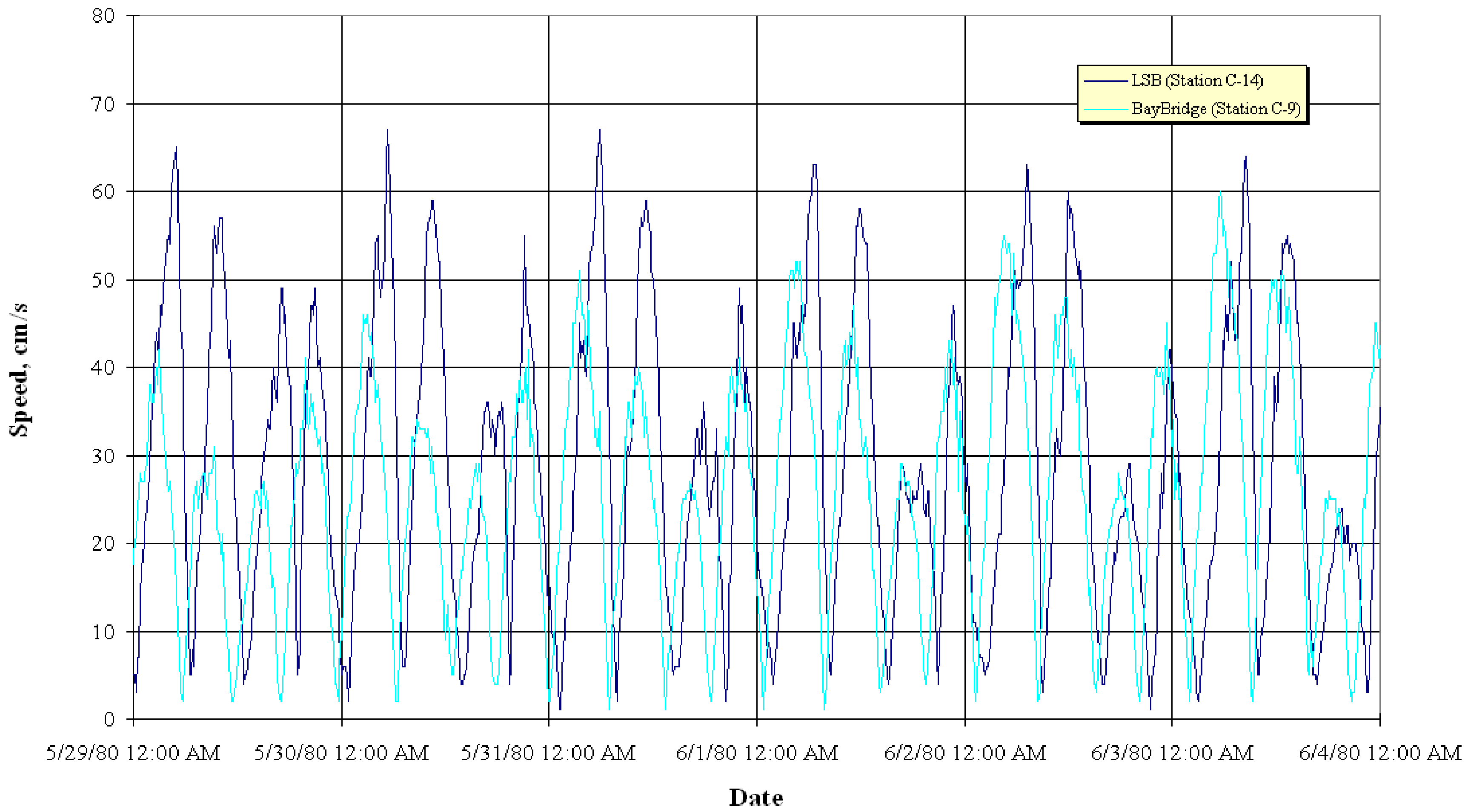


Figure 6-16. Tidal speeds at two locations in South San Francisco Bay.

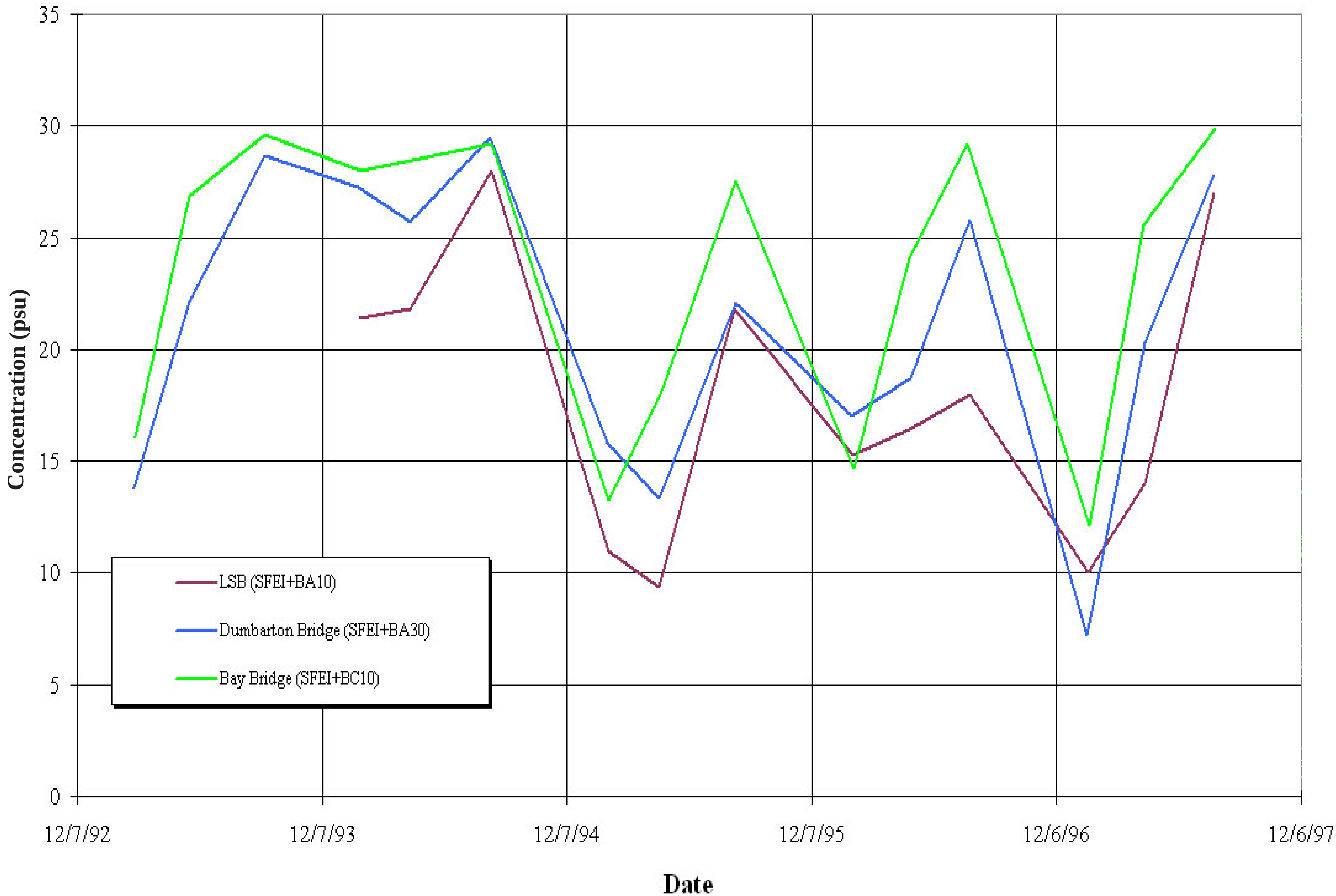


Figure 6-17a. Salinity vs. time at three South San Francisco Bay stations, using SFEI data.

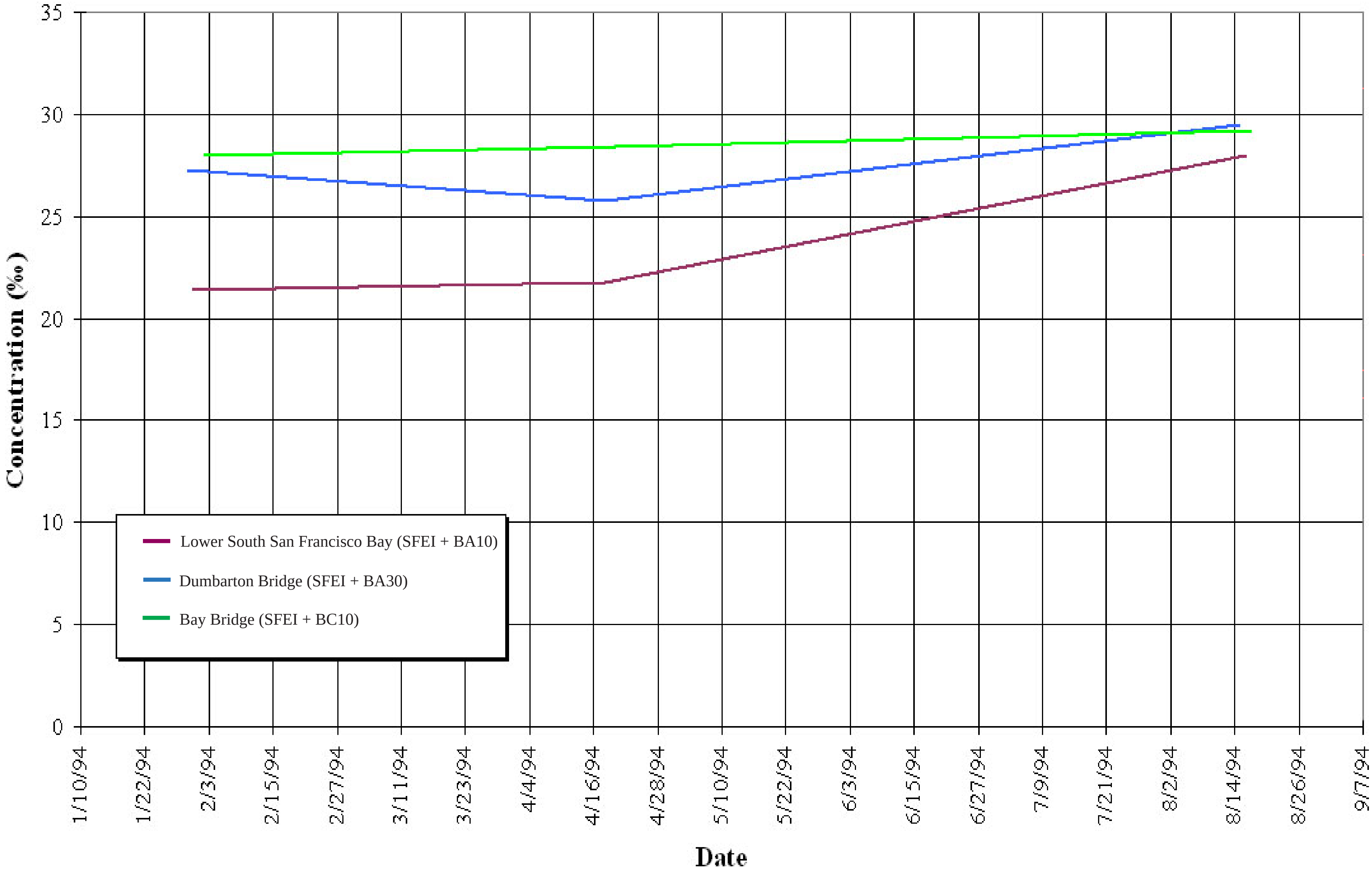


Figure 6-17b. Salinity vs. time over one year at three South San Francisco Bay stations.

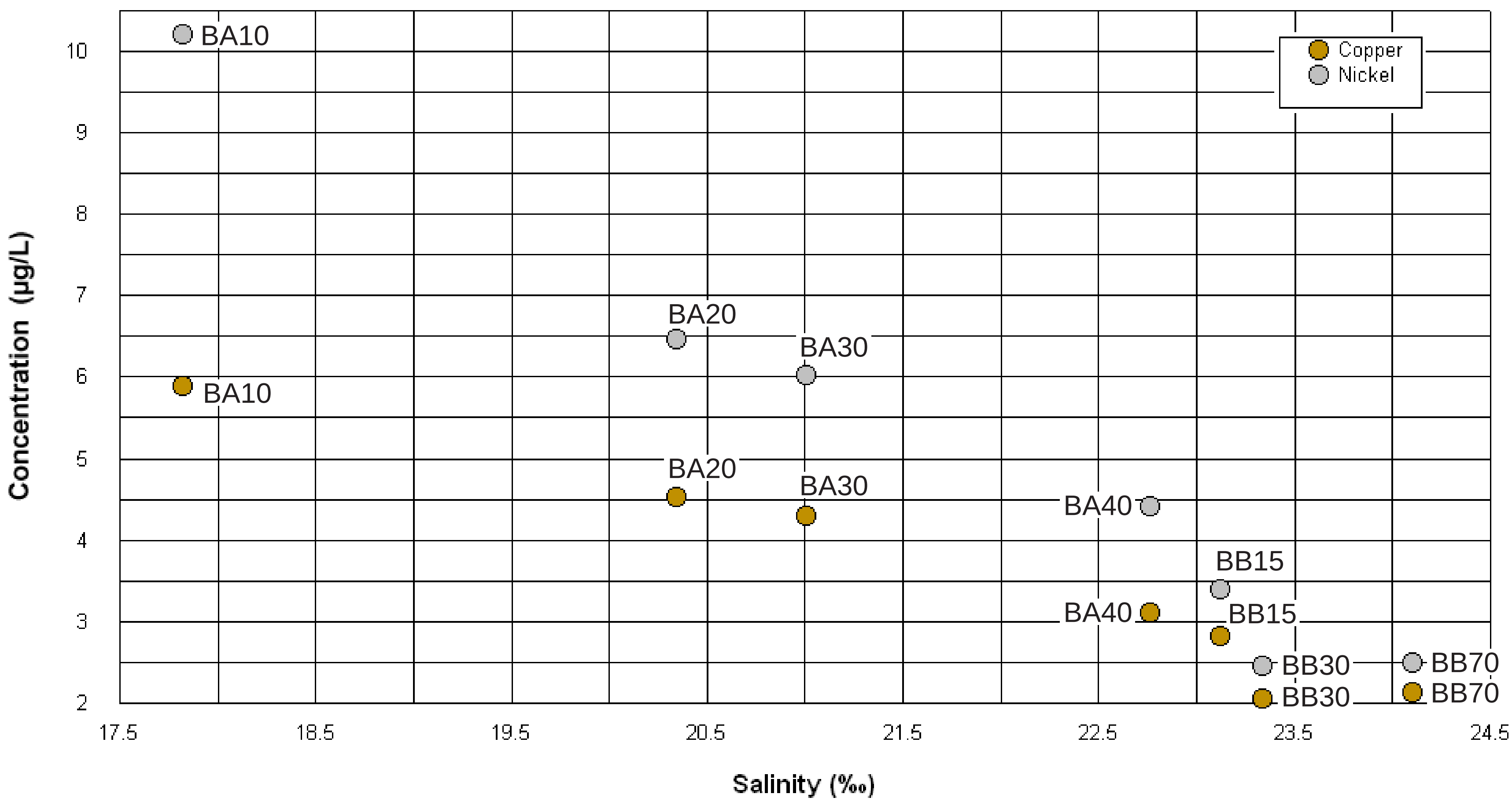


Figure 6-18a. Correlation between copper, nickel and salinity at locations within South San Francisco Bay.

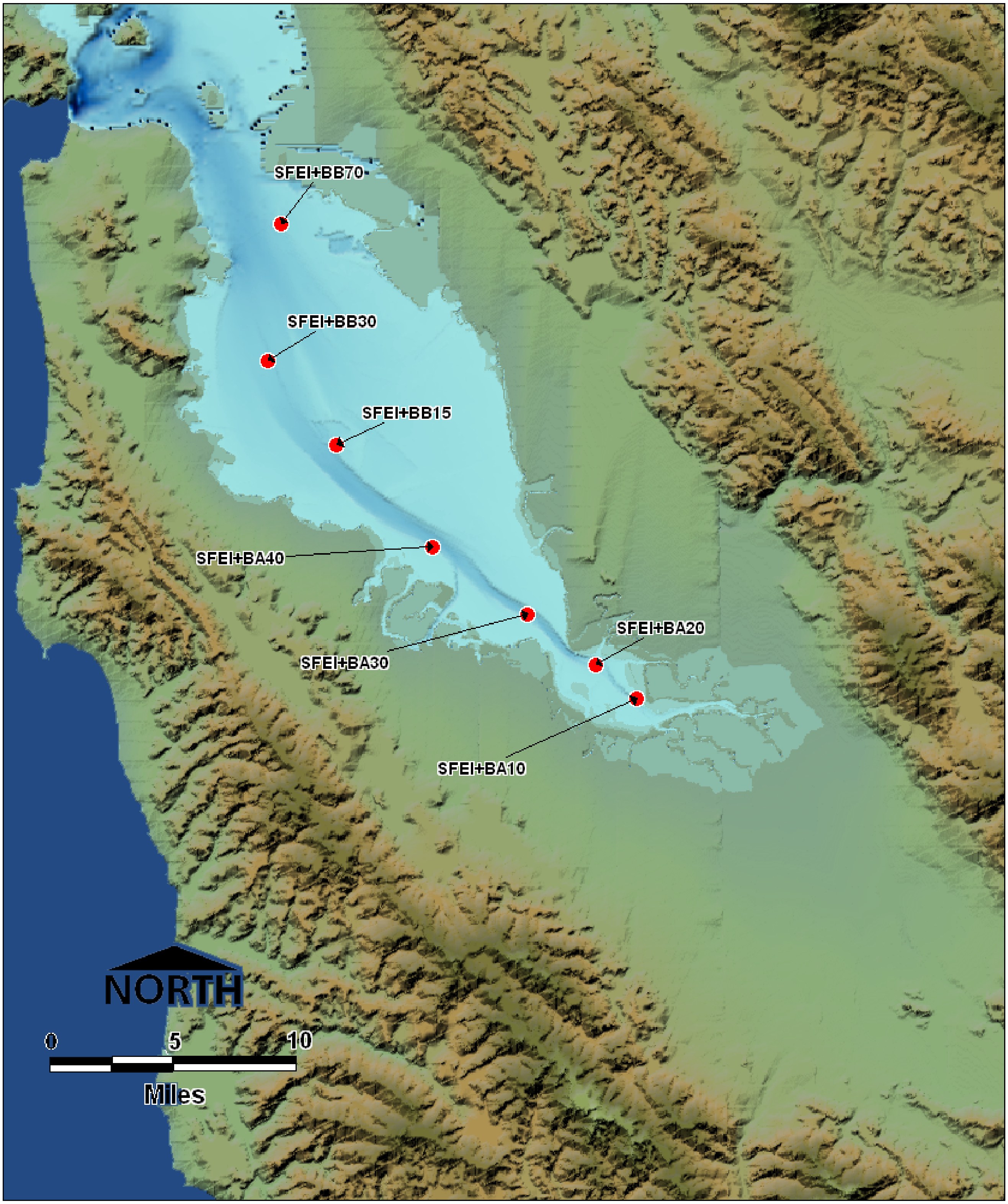


Figure 6-18b. Locations of monitoring stations used to develop correlations in Figure 6-18a.

7 CONCLUSIONS AND RECOMMENDATIONS

Several processes have been identified that would be important to the development of the TMDLs for copper and nickel, but for which there is either a lack of sufficient information or a high degree of uncertainty. These processes should be the focus of future studies. The major sources of uncertainties are summarized below, followed by recommendations for future studies to reduce these uncertainties.

7.1 Uncertainties

Sedimentation/Resuspension Dynamics - Interactions between the sediments and water column are important, both because metals released through resuspension and porewater diffusion are significant sources of metals to the water column and because external metal loads accumulate in the sediments and produce exposure through the benthic food web. Unfortunately, limited information is available on the sedimentation dynamics of the Lower South San Francisco Bay. A detailed sediment budget has not been developed. The magnitude, seasonal variations, and year to year variations of external sediment loads from the watersheds are highly uncertain due to limited data. Information on the temporal variations in sedimentation and resuspension fluxes is also sparse. No information is available on the exchange of sediments between the shoals and the channel. Understanding the differences in the sedimentation and resuspension dynamics between the shallow shoal areas and the deeper channel areas is important for quantifying resuspension fluxes and metals release to the water. No sedimentation or hydrodynamic data are currently available for the shallow areas south of the Dumbarton Bridge. Sediment rheology parameters such as erodability have also not been measured. Sediment transport processes and sediment exchange with regions north of the Lower South Bay have not been well quantified.

Adsorption/Desorption Kinetics - Desorption of copper and nickel during sediment resuspension is an important source of dissolved metals to the water column, yet very limited information is available on the rate constants for the adsorption and desorption reactions. These rates will vary depending on the size and nature of the suspended particles, so the particle size distributions of both suspended particles and sediments also need to be quantified.

Limited Sediment Core Data - Information on copper and nickel concentrations in sediments and sediment porewaters is limited to only a few cores and sampling dates. More data are necessary to better determine metal release fluxes due to resuspension and porewater diffusion, and to estimate the long-term sediment recovery from the previously higher historical loadings.

Nonpoint Source Tributary Loads - Wet season tributary loads of copper and nickel are currently the largest external sources, but their magnitudes and temporal variations have high uncertainties. The streams have not been regularly monitored for metals and suspended particle concentrations, so the loadings are based on simulation model predictions (URS Greiner Woodward Clyde, 1998). The resulting estimates are uncertain because the data used in the model have a high degree of variability, land-use data from the late 1980's were used, limited data were available for metal concentrations in runoff from open space and industrial land uses, large correction factors were required during model calibration, and several simplifying assumptions were made by the model (e.g., metal concentrations in runoff are independent of flow rates and antecedent conditions) (URS Greiner Woodward Clyde, 1998).

Metal Speciation - Limited information is available on the speciation of copper and nickel in South San Francisco Bay waters, tributaries, and POTW discharges. Speciation has been measured on a few occasions (Donat et al.,1994; Sedlak et al., 1997; Bedsworth and Sedlak, 1999), but knowledge of temporal variations in speciation and of the sources, cycling, and fate of organic ligands that control complexation and speciation is limited.

Biological Cycling in Sediments and Water Column - No information is available on the accumulation of copper and nickel in sediments due to settling phytoplankton, and the release of the metals back to the water column through decomposition and remineralization at the sediment-water interface. Copper and nickel concentrations have not been measured in San Francisco Bay phytoplankton. This makes estimates of phytoplankton uptake fluxes or sediment cycling fluxes uncertain. No information is available on the effects of benthic invertebrates on copper and nickel remineralization from suspended particles during filtration and digestion, and benthic bioturbation/irrigation effects on sediment release fluxes (biologically enhanced advection).

Food Web Transfer - With the exception of bivalves, copper and nickel have not been measured in higher trophic level organisms such as zooplankton and fish in South San Francisco Bay. This makes it difficult to estimate food web transfer of the metals and the relative contributions of water versus food uptake. Limited information is available in the literature on copper and nickel uptake rates from water, assimilation efficiencies from food, and depuration rates. Much less information is available for nickel than for copper. Most of the available data are for different species than those in San Francisco Bay. Although information from other species can be used to estimate uptake and accumulation of copper and nickel in South San Francisco Bay organisms, these estimates would be speculative without some measurements of copper and nickel concentrations in the target organisms and their key food sources. Although tissue concentration data are available for benthic bivalves, no data are available for their major food sources (phytoplankton, organic detritus).

Limited Information on Nickel - Much less is known about the cycling, bioavailability, uptake, accumulation, and toxicity of nickel than of copper. This is true of the literature in general, as well as for studies conducted specifically in San Francisco Bay.

Limited Wet Season Data - Less information is available for wet season cycling and transport processes than for the dry season. Most of the existing transport studies have focused on dry season conditions. The effects of seasonal variations in Delta outflows and flushing effects on the fate of copper and nickel in the Lower South San Francisco Bay are not known.

7.2 Recommendations for Additional Studies

The highest priority should be to quantify the speciation of copper and nickel and the cycling processes that influence speciation, since this determines bioavailability, uptake, and toxicity to aquatic organisms. If it is determined that the potential exists for the impairment of beneficial uses due to copper or nickel concentrations in Lower South San Francisco Bay, then steps should be taken to better quantify the sources of these metals. Four key areas have been identified for future studies: 1) biogeochemical processes influencing chemical speciation, 2) effects of speciation and competing metals on phytoplankton uptake and toxicity, 3) resuspension fluxes and other sediment-water interactions, and 4) wet season tributary loads.

7.2.1 Biogeochemical Processes Influencing Speciation

Additional studies should be considered to improve understanding of copper and nickel speciation in the South Bay. Only free metal ions and inorganic complexes are available for uptake by aquatic organisms, so these are the forms that determine toxicity. However, adsorbed forms and organic complexes make up a major portion of the total copper and nickel in the South Bay water column. Speciation of copper and nickel in South San Francisco Bay have been characterized in both the water column (Donat et al., 1994) and in tributary runoff and POTW loads (Sedlak et al., 1997; Bedsworth and Sedlak, 1999). Complexation with organic ligands plays a major role in the speciation. The ligands can be separated into two major classes, very strong ligands and weaker ligands. The sources and nature of the ligands in external loads have been characterized (Sedlak et al., 1997; Bedsworth and Sedlak, 1999). However, little is known about internal sources of ligands and the internal cycling and fate of organic ligands within the Bay, and how future changes in the discharge of these ligands could affect the complexation and speciation of the metals. The kinetics of the complexation reactions may also be important, since the slow kinetics suggested by Sedlak et al. (1997) and Bedsworth and Sedlak (1999) for the strong ligand classes may prevent the use of equilibrium-based geochemical models for accurate predictions of speciation. As a result of these uncertainties, studies that improve our ability to predict speciation and bioavailability as conditions in the water column change should receive high priority. This will most likely involve a combination of field, laboratory, and model analyses. The adsorption/desorption processes that influence speciation will be addressed by the recommended sediment resuspension studies.

7.2.2 Effects of Speciation and Competing Metals on Phytoplankton Uptake and Toxicity

Phytoplankton are among the most sensitive organisms to copper toxicity and are an important consideration in the Impairment Assessment. However, little direct information is available on the uptake, accumulation, and toxicity of copper and nickel to phytoplankton under the specific water quality and speciation conditions in Lower South San Francisco Bay. Complexation with organics reduces the bioavailability of copper and nickel, and competitive interactions with other metals and possibly other cations could reduce uptake and toxicity. These factors can be addressed empirically through the use of water effect ratio (WER) experiments. However, WER experiments do not provide sufficient information to predict how uptake and toxicity could change as a result of seasonal or long-term variations in the cycling of organic ligands and competing metals. Copper and nickel concentrations in South Bay phytoplankton have not been measured due to the practical difficulty of separating them from other suspended particles, which are more abundant. This makes it difficult to estimate the effects of phytoplankton on the biogeochemical cycling of copper and nickel in the Lower South Bay, and to estimate trophic transfer to consumer organisms such as zooplankton and benthic invertebrates.

Phytoplankton uptake and toxicity studies should be conducted using Lower South Bay water and representative phytoplankton species to assess the effects of speciation and competing metals on uptake and toxicity. Such studies should be conducted over a range of conditions that represent current seasonal cycles, as well as possible future conditions. These experiments could also provide estimates of copper and nickel concentrations in phytoplankton cells that could be used to estimate biological effects on copper and nickel cycling, and to estimate trophic transfer to higher organisms.

7.2.3 Resuspension Fluxes and Other Sediment-Water Interactions

One of the largest sources of both dissolved and particulate copper and nickel is estimated to be resuspension from the sediments. Although external loads are highest during the wet season, water column concentrations of both dissolved and particulate copper and nickel are highest during the dry season. The dry season is also the windy season, when resuspension rates are highest. During sediment resuspension, desorption can release significant quantities of dissolved metals to the water column. Mass balance analyses of dry season loadings, inventories, and residence times in the water column of the Lower South Bay indicate that desorption during resuspension could be a major source of dissolved copper and nickel during the dry season. The other loadings cannot account for the currently observed dissolved metal concentrations in the water column. This internal source is also the most difficult to quantify, and therefore has the highest uncertainty and the least amount of information available. Decomposition and mineralization of settled phytoplankton could also be an important sediment source, as could remineralization of suspended particles during benthic grazing and benthic bioturbation/irrigation effects on sediment release.

Therefore, studies to better quantify copper and nickel release during resuspension and biological effects on sediment cycling are recommended. Of related importance are studies to quantify the accumulation of metals into the sediments. Since the sediments are a main repository of both historical and continuing loads, and since they continue to reintroduce copper and nickel into the water column through resuspension, sediment diffusion, and biological cycling, it would be useful to get a better understanding of the movement of copper and nickel into the sediments from existing external loading sources. It may be appropriate to convene an expert panel to develop ideas for further studies to quantify these processes. Laboratory experiments should be conducted to estimate desorption fluxes using surficial sediments and water collected from the Lower South Bay. Since the metal concentrations adsorbed to particles appear to vary with particle size, additional information to establish these relationships, along with particle size distributions in the Lower South Bay, should be established through field and/or laboratory studies. This information should be used in conjunction with model analyses to estimate the resuspension and other sediment exchange fluxes, since it is not practical to obtain direct estimates from field studies. Ongoing studies by Moss Landing Marine Laboratories (MLML) of soluble metal fluxes from the sediments could be used to refine the current estimates of these fluxes. Analysis of historical bathymetry changes along with geochemical studies of sediment cores could provide additional information on metal accumulation in sediments.

7.2.4 Wet Season Tributary Loads

Wet season tributary runoff loads are the most important of the external load sources, both in terms of magnitude and in terms of potential for load reductions by watershed management or stormwater treatment. The existing load estimates also have a fair amount of uncertainty associated with them, and they could be refined using more current or projected land use information, more recent and complete runoff loading data, and more advanced models than were available when the original estimates were made. Therefore, these loads should be the primary focus of additional work on refining external load estimates. POTW loads have already been substantially reduced and the load estimates are well characterized through frequent monitoring. Atmospheric loads are uncertain, but are very small compared to other sources and therefore do not merit additional work. Sediment diffusion loads appear to be small relative to resuspension loads. However, these estimates were based on limited data, and they should be refined in conjunction with the other sediment studies recommended above. Even though the wet season tributary loads occur during the period when water column concentrations of copper and nickel are at their lowest, they are still the largest external source, and therefore probably contribute significantly to the sediment inventories, which in turn contribute to the water column through resuspension during the dry season.

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APPENDIX A

ABIOTIC COMPONENT OF COPPER AND NICKEL CYCLING AND SPECIATION

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A.1 Introduction

In this section, computations are provided to estimate how copper and nickel are likely to be speciated within the water column of Lower South San Francisco Bay. Both equilibrium and rate-limited reactions are shown, as appropriate. Two alternative abiotic cycling models are developed. The two alternative models are shown because it appears that data to implement kinetically-limited reactions between strong complexing ligands and copper and nickel are not presently available. Such data would need to be collected to implement the more complex model.

A.2 Copper

A.2.1 Composite Species

Begin by defining species. Refer to Figure A-1.

Sum of Dissolved Inorganic Species (C_{in}):

$$C_{in} = Cu^{++} + Cu(OH)_2 + CuSO_4^0 + CuCO_3^0 + CuCl^+ + Cu(OH)^+$$

Total Dissolved (C_d):

$$C_d = C_{in} + Cu - L_1 + Cu - L_2$$

Total Dissolved and Adsorbed (C_T):

$$C_T = C_d + Cu^{++} - S$$

A.2.2 Equilibrium Reactions (MINTEQ Simulation Results of Very Fast Reactions Only)

$$\frac{Cu^{++}}{C_{in}} = \begin{cases} 0.048, \text{dry season(salinity ~ 33 practical salinity units(psu))} \\ 0.023, \text{wet season(salinity ~ 5psu, This is a lower limit of salinity that might occur} \\ \text{only during very wet years.)} \end{cases}$$

$$\frac{CuSO_4^0}{C_{in}} = \begin{cases} 0.011, \text{dryseason} \\ 0.006, \text{wetseason} \end{cases}$$

$$\frac{CuCO_3^0}{C_{in}} = \begin{cases} 0.148, \text{dryseason} \\ 0.198, \text{wetseason} \end{cases}$$

$$\frac{CuCl^+}{C_{in}} = \begin{cases} 0.01, \text{dryseason} \\ 0.001, \text{wetseason} \end{cases}$$

$$\frac{Cu(OH)_2}{C_{in}} = \begin{cases} 0.768, \text{dryseason} \\ 0.758, \text{wetseason} \end{cases}$$

Note: Other minor species with less than one percent contribution, such as $Cu(OH)^+$ may also exist. This explains why the sum of the fractions are slightly less than 1.0.

A.2.3 Rate-Limited Reactions

Adsorption-Desorption: $Cu^{++} + S \rightleftharpoons Cu^{++} - S$

$$R_f^s = k_f^s \times Cu^{++} \times S \qquad k_f^s \approx 10^{0.28}\,\ell mg^{-1}h^{-1} \text{ (Wood et al. 1995)}$$

$$R_b^s = k_b^s \times Cu^{++} - S \qquad k_b^s \approx 10^{-1.4}\,h^{-1} \text{ (Wood et al. 1995)}$$

At equilibrium: $R_f^s = R_b^s$ (in Lower South San Francisco Bay, equilibrium may not occur; however the concept of an equilibrium partition coefficient is useful and frequently reported in the literature).

Or: $$K_p = \frac{Cu^{++}}{C_d} \times \frac{k_f^s}{k_b} \qquad K_p \approx 15{,}000\,\ell/\text{kg, or higher (this report)}$$

(See also Wood et al, 1995, Fig. 1)

Ligand 1: $Cu^{++} + L_1 \rightleftharpoons Cu - L_1$

$$R_f^{L_1} = k_f^{L_1} \times Cu^{++} \times L_1 \qquad k_f^{L_1} : \text{unknown}$$

$$L_1 : \text{unknown}$$

$$R_b^{L_1} = k_b^{L_1} \times (Cu - L_1) \qquad k_b^{L_1} : \text{unknown}$$

Ligand 2: $Cu^{++} + L_2 \rightleftharpoons Cu - L_2$

$$R_f^{L_2} = k_f^{L_2} \times Cu^{++} \times L_2 \qquad k_f^{L_2} : \text{unknown}$$

$$L_2 : \text{unknown}$$

$$R_b^{L_2} = k_b^{L_2} \times (Cu - L_2) \qquad k_b^{L_2} : \text{unknown}$$

A.3 Nickel

For nickel, refer to Figure A-2.

A.3.1 Composite Species

Sum of Dissolved Inorganic Species (C_{in}):

$$C_{in} = Ni^{++} + NiCl^{+} + NiSO_4^0 + NiCl_2^0 + NiCO_3^0 + Ni(CO_3^0)_2^{=}$$

Total Dissolved (C_d):

$$C_d = C_{in} + Ni - L_1 + Ni - L_2$$

Total Dissolved and Adsorbed (C_T):

$$C_T = C_d + Ni^{++} - S$$

A.3.2 Equilibrium Reactions (MINTEQ Simulation Results)

$$\frac{Ni^{++}}{C_{in}} = \begin{cases} 0.15, \text{ dry season } (\text{Salinity} = 33 \text{ psu}) \\ 0.08, \text{ wet season } (\text{Salinity} = 5 \text{ psu}) \end{cases}$$

$$\frac{NiCl^{+}}{C_{in}} = \begin{cases} 0.048, \text{ dry season} \\ 0.02, \text{ wet season} \end{cases}$$

$$\frac{NiSO_4^{o}}{C_{in}} = \begin{cases} 0.015, \text{ dry season} \\ 0.01, \text{ wet season} \end{cases}$$

$$\frac{NiCl_2}{C_{in}} = \begin{cases} 0.036, \text{ dry season} \\ 0.01, \text{ wet season} \end{cases}$$

$$\frac{NiCO_3^{o}}{C_{in}} = \begin{cases} 0.726, \text{ dry season} \\ 0.88, \text{ wet season} \end{cases}$$

$$\frac{Ni(CO_3^{o})_2}{C_{in}} = \begin{cases} 0.016, \text{ dry season} \\ 0.01, \text{ wet season} \end{cases}$$

Note: Other minor species may exist that contribute insignificant amounts to the total inorganic species.

A.3.3 Rate Limited Reactions

Adsorption-Desorption: $Ni^{++} + S \rightleftharpoons Ni^{++} - S$

$$R_f^s = k_f^s \times Ni^{++} \times S \qquad k_f^s: \text{unknown}$$

$$R_b^s = k_b^s \times (Ni^{++} - S) \qquad k_b^s: \text{unknown}$$

At equilibrium: $R_f^s = R_b^s$ (in Lower South Bay, equilibrium may not occur; however the concept of an equilibrium partitioning coefficient is useful).

Or: $$K_p = \frac{Ni^{++}}{C_d}\frac{k_f^s}{k_b^s} \qquad K_p \approx 45{,}000\ \ell/\text{kg, or higher (this report)}$$

Ligand 1: $Ni^{++} + L_1 \rightleftharpoons Ni - L_1$

$$R_f^{L_1} = k_f^{L_1} \times Ni^{++} \times L_1 \qquad k_f^{L_1}: \text{unknown}$$

$$L_1: \text{unknown} \begin{pmatrix}\text{thought to be EDTA,} \\ \text{Bedsworth and Sedlak, 1999}\end{pmatrix}$$

$$R_b^{L_1} = k_b^{L_1} \times (Ni - L_2) \qquad k_b^{L_1}: \text{unknown}$$

Ligand 2: $Ni^{++} + L_2 \rightleftharpoons Ni - L_2$

$$R_f^{L_2} = k_f^{L_2} \times Ni^{++} \times L_2 \qquad k_f^{L_2}: \text{unknown}$$

$$k_b^{L_2}: \text{unknown}$$

$$R_b^{L_2} = k_b^{L_2} \times (Ni - L_2) \qquad L_2: \text{unknown}$$

A.4 Simplified Abiotic Cycling Models

Given the limited amount of rate constant data for the L_1 and L_2 speciation reactions that are currently available, a more simplified but less technically justifiable abiotic cycling/speciation model is shown in Figure A-3 for copper and Figure A-4 for nickel. This model assumes an equilibrium between the free ions (Cu^{++} and N^{++}) and the strong/weak ligands. Assuming the ratios of free ion to L_1 and L_2 complexes are known and are constants, this model can be implemented without knowledge of the (at present) unknown rate constants. These simplified models are presented as an alternative to the more complex models in Figures A-1 and A-2. However, their applicability to Lower South San Francisco Bay is uncertain at present.

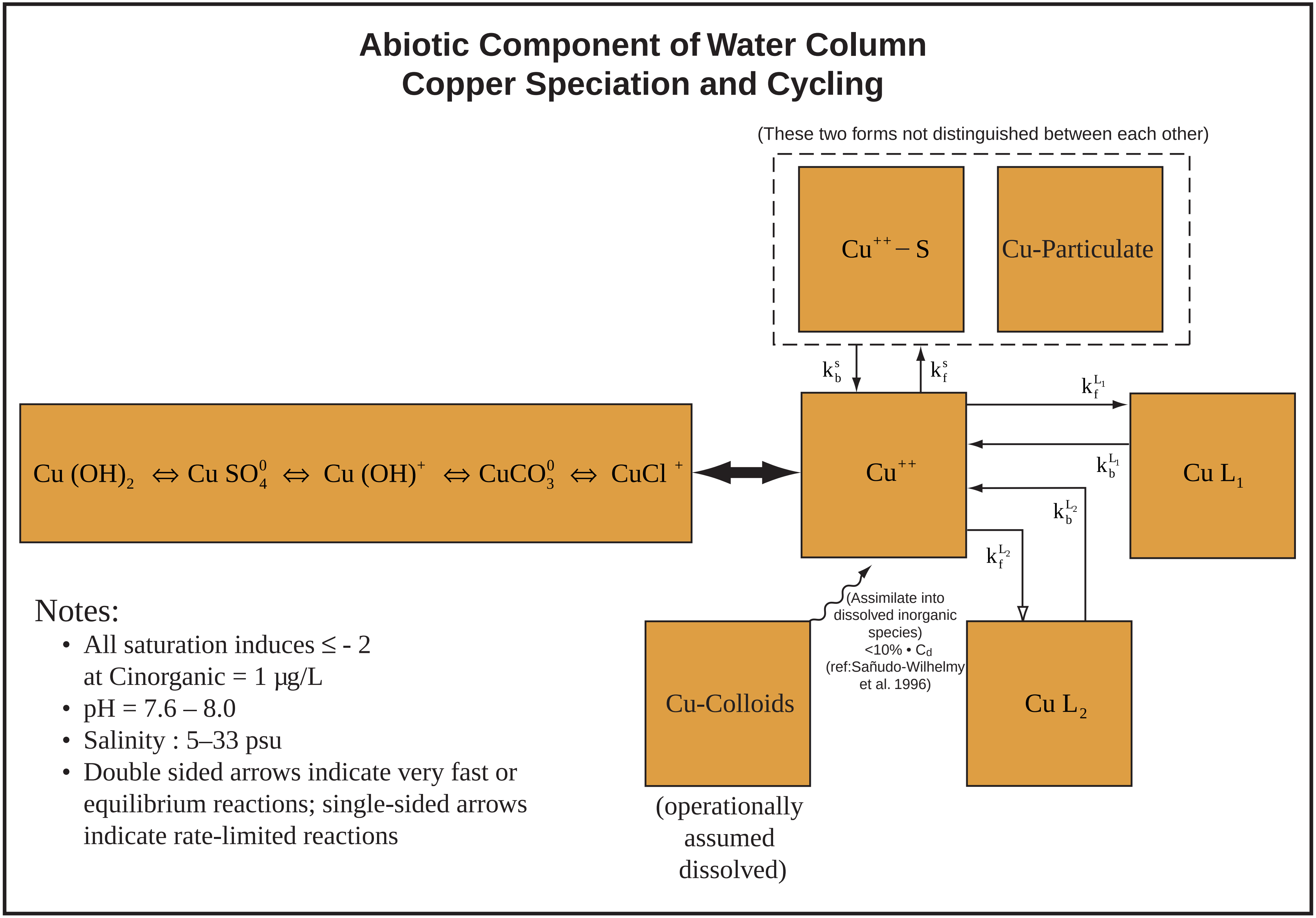


Figure A-1. Abiotic component of water column copper speciation and cycling.

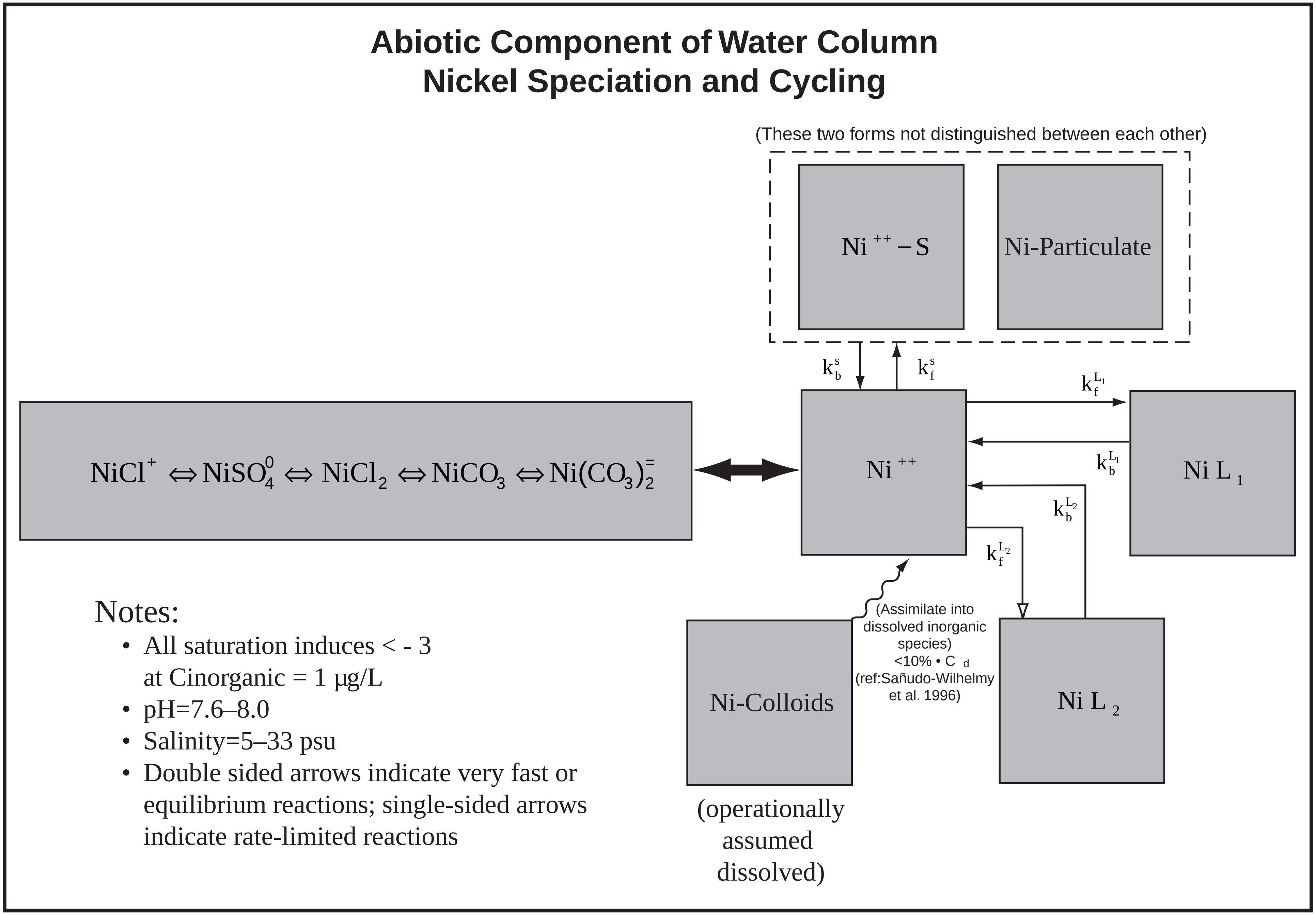
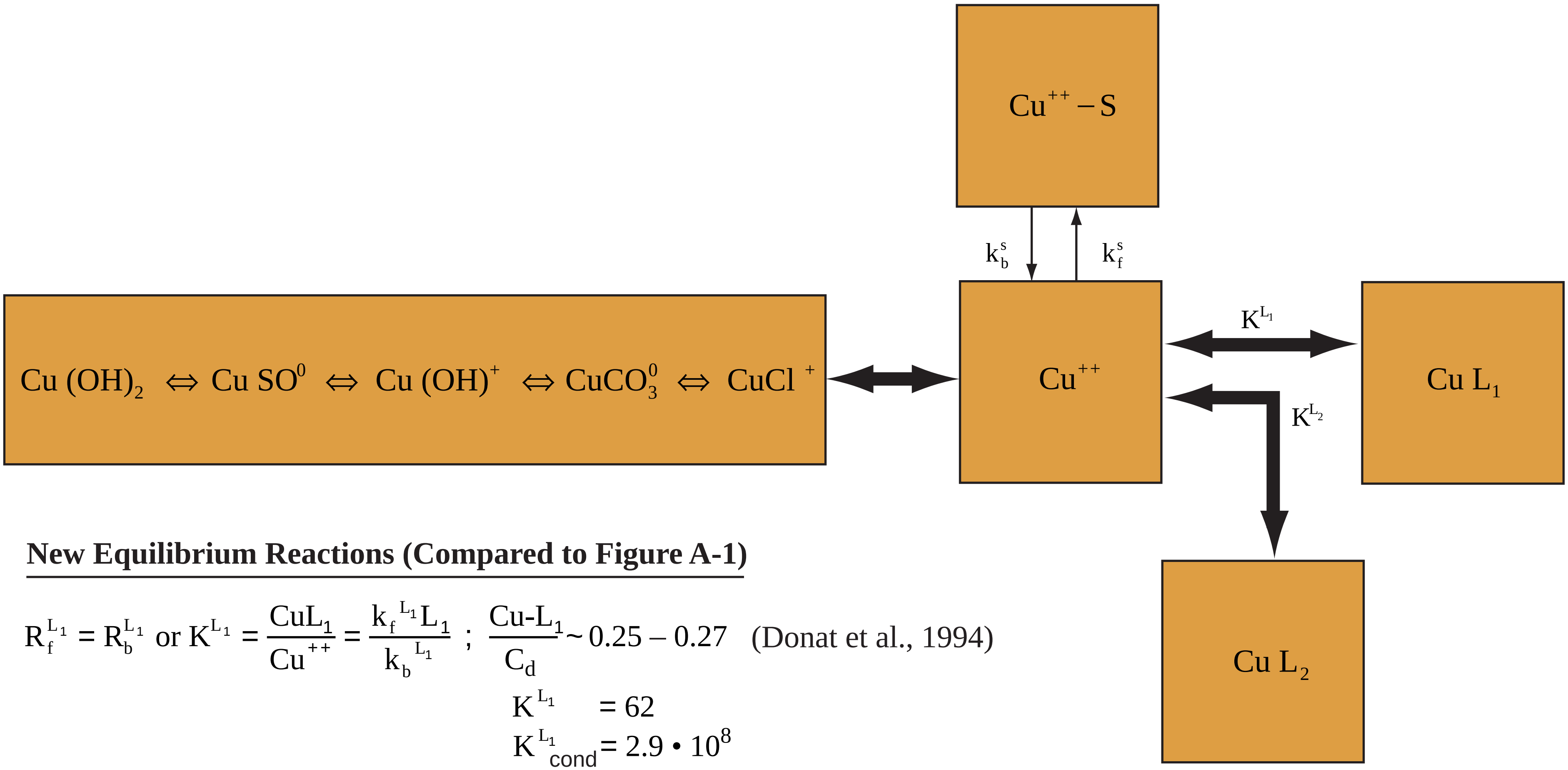


Figure A-2. Abiotic component of water column nickel speciation and cycling.

Simplified Abiotic Copper Speciation Diagram



New Equilibrium Reactions (Compared to Figure A-1)

$$R_f^{L_1} = R_b^{L_1} \text{ or } K^{L_1} = \frac{CuL_1}{Cu^{++}} = \frac{k_f^{L_1} L_1}{k_b^{L_1}} \;;\; \frac{Cu\text{-}L_1}{C_d} \sim 0.25 - 0.27 \quad \text{(Donat et al., 1994)}$$

$$K^{L_1} = 62$$

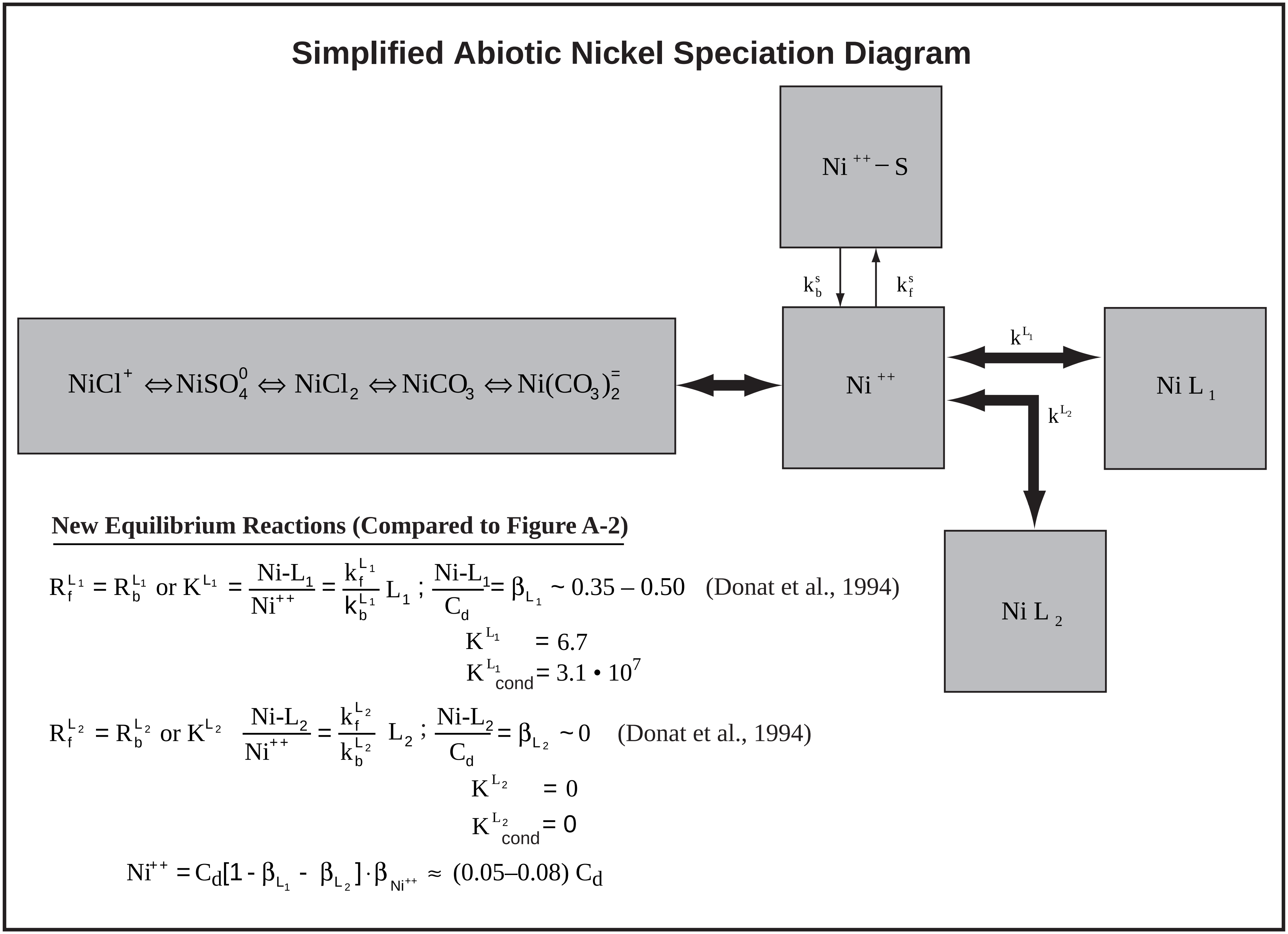
$$K^{L_1}_{cond} = 2.9 \bullet 10^8$$

$$R_f^{L_2} = R_b^{L_2} \text{ or } K^{L_2} = \frac{Cu\text{-}L_2}{Cu^{++}} = \frac{k_f^{L_2} L_2}{K_b^{L_2}} \;;\; \frac{Cu\text{-}L_2}{C_d} \sim 0.52 - 0.65 \quad \text{(Donat et al., 1994)}$$

$$K^{L_2} = 140$$

$$K^{L_2}_{cond} = 2.0 \bullet 10^6$$

Figure A-3. Simplified abiotic copper speciation diagram.



New Equilibrium Reactions (Compared to Figure A-2)

$$R_f^{L_1} = R_b^{L_1} \text{ or } K^{L_1} = \frac{\text{Ni-L}_1}{Ni^{++}} = \frac{k_f^{L_1}}{k_b^{L_1}} L_1 \;;\; \frac{\text{Ni-L}_1}{C_d} = \beta_{L_1} \sim 0.35 - 0.50 \quad \text{(Donat et al., 1994)}$$

$$K^{L_1} = 6.7$$

$$K^{L_1}_{cond} = 3.1 \bullet 10^7$$

$$R_f^{L_2} = R_b^{L_2} \text{ or } K^{L_2} \; \frac{\text{Ni-L}_2}{Ni^{++}} = \frac{k_f^{L_2}}{k_b^{L_2}} L_2 \;;\; \frac{\text{Ni-L}_2}{C_d} = \beta_{L_2} \sim 0 \quad \text{(Donat et al., 1994)}$$

$$K^{L_2} = 0$$

$$K^{L_2}_{cond} = 0$$

$$Ni^{++} = C_d[1 - \beta_{L_1} - \beta_{L_2}] \cdot \beta_{Ni^{++}} \approx (0.05–0.08)\ C_d$$

Figure A-4. Simplified abiotic nickel speciation diagram.

APPENDIX B

COPPER AND NICKEL

FLUX CALCULATIONS

B.1 Excel Spreadsheets with Algorithms, Data and Results of the Flux Calculations shown in Figures 2-3 and 2-5

An Excel spreadsheet was created to perform the calculations shown in Figures 2-3 and 2-5. All algorithms, data input, and results are shown below for copper and nickel for dry and wet seasons. A sensitivity analysis is provided at the end. To generate a range of estimates for Figures 2-3 and 2-5, two sets of background stations were used: BB30 and the average of BA30 and BA40. The results in this appendix, though, are for one background location (BB30). In general, it is expected that the approach used will generate particulate fluxes from the bed that are closer to the upper end of the range.

Algorithm

(1) Flux Past Dumbarton Bridge (kg/dry-season or kg/wet-season)

(1-a) Dissolved Flux:

$$\frac{(C_d - C_{db}) \cdot V_{LSB}}{\tau} \cdot 10^{-6} \cdot \frac{365.25}{2}$$

(1-b) Total Flux:

$$\frac{(C_T - C_{Tb}) \cdot V_{LSB}}{\tau} \cdot 10^{-6} \cdot \frac{365.25}{2}$$

(2) Particulate Flux:

(2-a) Copper, dry season:

$$F^{Cu}_{particulate-bed} = Total\ \ flux\ \ past\ \ Dumbarton\, Bridge - \sum Total\ \ fluxes\, in$$

(2-b) Nickel, dry season:

$$F^{Ni}_{particulate-bed} = \frac{X^{Ni}_{bed}}{X^{Cu}_{bed}} \cdot F^{Cu}_{particulate-bed}$$

(2-c) Copper, wet season:

$$F^{Cu}_{particulate-wet} = \left(\frac{X^{Cu}_{wet}}{X^{Cu}_{dry}}\right)\left(\frac{TSS_{wet}}{TSS_{dry}}\right)\left(\frac{\tau_{dry}}{\tau_{wet}}\right) \cdot F^{Cu}_{particulate-dry}$$

(2-d) Nickel, wet season:

$$F^{Ni}_{particulate-wet} = \frac{\mathrm{X}^{\mathrm{Ni}}_{\mathrm{wet}}}{\mathrm{X}^{\mathrm{Cu}}_{\mathrm{wet}}} \cdot F^{Cu}_{particulate-wet}$$

(3) Internal Cycling of Dissolved Copper/Nickel:

$$\boldsymbol{F^{internal}_{dissolved} = Dissolved\ \ flux\ \ past\ \ Dumbarton\ \ Bridge - \Sigma\ Dissolved\ \ fluxes\ \ in}$$

(4) Mass in Bed (kg)

$$\boldsymbol{Mass = \frac{V_{LSB}}{H} \cdot T \cdot \rho \cdot X} \cdot 10^{-6}$$

$$\boldsymbol{Mass\ \ Above\ \ Background = \frac{V_{LSB}}{H} \cdot T \cdot \rho \cdot (X - X_{background})} \cdot 10^{-6}$$

(5) Post-Processing

(5a) Total suspended solids concentration (mg/L) that results from particulate flux from bed

Dry Season: $$TSS_{dry} = \frac{F^{Cu}_{particulate-bed-dry} \cdot \tau_{dry} \cdot 10^9}{X^{Cu}_{dry} \cdot V_{LSB} \cdot (365.25/2)}$$

Wet Season: $$TSS_{wet} = \frac{F^{Cu}_{particulate-bed-wet} \cdot \tau_{wet} \cdot 10^9}{X^{Cu}_{wet} \cdot V_{LSB} \cdot (365.25/2)}$$

(5b) Concentration contributions by source (by dry & wet seasons)

Dissolved (ug/L)

$$C_i = \frac{M_i^{dissolved} \cdot \tau \cdot 10^6}{V \cdot (365.25/2)}$$

Total (ug/L)

$$C_i = \frac{M_i^{total} \cdot \tau \cdot 10^6}{V \cdot (365.25/2)}$$

i: point
atmospheric
diffusive
tributaries
bed-particulate

GENERAL DRY SEASON INFORMATION

τ	=	20	**flushing time, days**	
V_{LSB}	=	8.60E+07	**volume, m^3**	
TSS	=	75	**mg/L at station**	SB02
TSS_b	=	40	**mg/L, background at station**	near San Mateo Bridge
H	=	2.6	**m, mean depth in LSB**	

GENERAL WET SEASON INFORMATION

τ	=	20	**flushing time, days**	
V_{LSB}	=	8.60E+07	**volume, m^3**	
TSS	=	59	**mg/L at station**	SB02
TSS_b	=	35	**mg/L, background at station**	near San Mateo Bridge
H	=	2.6	**m, mean depth in LSB**	

DRY SEASON COPPER CALCULATIONS

INPUT DATA FOR FLUX CALCULATIONS IN LOWER SOUTH SAN FRANCISCO BAY

------------------------- DRY SEASON (1 June through 30 November) -------------------------

Water: **Copper**

Dissolved, ug/L					Total, ug/L					
C_d =	3.3	@	Station	BA20/SB02	C_T =	12.3	@	Station	BA20/SB02	
C_{db} =	1.8	@	Station	BB30	C_{Tb} =	2.2	@	Station	BB30	(Used for calculations)
C_{db} =	2.6	@	Station	BA40/BA30	C_{Tb} =	3.2	@	Station	BA40/BA3(	(used for reference only)

Sediment Bed: **Copper**

X_{bed} = 39 mg/kg at station BA21

$X_{background}$ = 25 mg/kg at station NR San Mateo Bridge

T = Thickness for mass calculation = 1 m

ρ = Bulk density = 1400 kg/m^3

External Total Copper Loadings, kg/dry-season

M_{Point}	500
M_{Trib}	160
$M_{Diff\ Sed}$	110
M_{Atm}	60
$M_{Particulate\text{-}bed}$	to be calculated

RESULTS - COPPER (DRY SEASON)

------------------ Dry Season (1 June through 30 November) -------------------

Total Copper Fluxes, kg/dry-season

Fluxes into LSB			Fluxes Out	
Point	500		Past Dumbarton Bridge	7931
Atmospheric	60			
Diffusive	110			
Tributaries	160			
Bed-Particulate	7101	(calculated)		
Sum	7931			

Flux Balance: $$\frac{In - Out}{(In + Out)/2} = 0.000$$

Dissolved Copper Fluxes, kg/dry-season

Fluxes into LSB		Fluxes Out	
Point	400	Past Dumbarton Bridge	1178
Atmospheric	0		
Diffusive	110		
Tributaries	130		
Bed-Particulate	0		
Sum	640		

Flux Balance: $$\frac{In - Out}{(In + Out)/2} = -0.592$$

Internal Cycling of Copper to Close Flux Balance: 538

Mass in Sediments, kg

Total Mass	1.81E+06
Background Mass	1.16E+06
Excess (above background)	6.48E+05

Concentration Contributions by Source, ug/L

	Dissolved	Total
C_b	1.8	2.2
C_{point}	0.51	0.64
C_{atm}	0.00	0.08
$C_{diffusive}$	0.14	0.14
$C_{tributaries}$	0.17	0.20
$C_{bed\text{-}particulate}$	0.00	9.04
$C_{cycling\ sum}$	0.69	

TSS_{dry}= 231.87 **mg/L**

DRY SEASON NICKEL CALCULATIONS

INPUT DATA FOR FLUX CALCULATIONS IN LOWER SOUTH SAN FRANCISCO BAY

------------------------- DRY SEASON (1 June through 30 November) -------------------------

Water: **Nickel**

Dissolved, ug/L					Total, ug/L					
C_d =	3.8	@	Station	SB02	C_T =	23.8	@	Station	SB02	
C_{db} =	1.6	@	Station	BB30	C_{Tb} =	2.5	@	Station	BB30	(used for calculations)
C_{db} =	2.6	@	Station	BA40/BA30	C_{Tb} =	5.2	@	Station	BA40/BA3(	(used for reference only)

Sediment Bed: **Nickel**

X_{bed} = 99 mg/kg at station BA21

$X_{background}$ = 90 mg/kg at station NR San Mateo Bridge

T = Thickness for mass calculation = 1 m

ρ = Bulk density = 1400 kg/m^3

External Total Nickel Loadings, kg/dry-season

M_{Point}	800
M_{Trib}	40
$M_{Diff\ Sed}$	360
M_{Atm}	15
$M_{Particulate\text{-}bed}$	to be calculated

RESULTS - NICKEL (DRY SEASON)

------------------ Dry Season (1 June through 30 November) -------------------

Total Nickel Fluxes, kg/dry-season

Fluxes into LSB			**Fluxes Out**	
Point	800		Past Dumbarton Bridge	1.67E+04
Atmospheric	15			
Diffusive	360			
Tributaries	40			
Bed-Particulate	18027	(calculated)		
Sum	19242			

Flux Balance: $$\frac{In - Out}{(In + Out)/2}$$ = 0.140

Dissolved Nickel Fluxes, kg/dry-season

Fluxes into LSB		**Fluxes Out**	
Point	640	Past Dumbarton Bridge	1728
Atmospheric	0		
Diffusive	360		
Tributaries	32		
Bed-Particulate	0		
Sum	1032		

Flux Balance: $$\frac{In - Out}{(In + Out)/2}$$ = -0.504

Internal Cycling of Nickel to Close Flux Balance: 696

Mass in Sediments, kg

Total Mass	4.58E+06
Background Mass	4.17E+06
Excess (above background)	4.17E+05

Concentration Contributions by Source, ug/L

	Dissolved	Total
C_b	1.6	2.5
C_{point}	0.81	1.02
C_{atm}	0.00	0.02
$C_{diffusive}$	0.46	0.46
$C_{tributaries}$	0.04	0.05
$C_{bed\text{-}particulate}$	0.00	22.96
$C_{cycling\ sum}$	0.886	

TSS_{dry}= 231.87 **mg/L**

WET SEASON COPPER CALCULATIONS

INPUT DATA FOR FLUX CALCULATIONS IN LOWER SOUTH SAN FRANCISCO BAY

------------------------- WET SEASON (1 December through 31 May) -------------------------

Water: **Copper**

Dissolved, ug/L					Total, ug/L					
C_d =	2.4	@	Station	BA20	C_T =	10.7	@	Station	BA20	
C_{db} =	1.6	@	Station	BB30	C_{Tb} =	2.1	@	Station	BB30	(used for calculations)
C_{db} =	2.6	@	Station	BA40/BA30	C_{Tb} =	3.7	@	Station	BA40/30	(used for reference only)

Sediment Bed: **Copper**

X_{bed} = 41 mg/kg at station BA21

$X_{background}$ = 25 mg/kg at station NR San Mateo Bridge

T = Thickness for mass calculation = 1 m

ρ = Bulk density = 1400 kg/m^3

External Total Copper Loadings, kg/wet-season

M_{Point}	700
M_{Trib}	3600
$M_{Diff\ Sed}$	110
M_{Atm}	60
$M_{Particulate\text{-}bed}$	to be calculated

RESULTS - COPPER (WET SEASON)

----------------- WET SEASON (1 December through 31 May) -------------------

Total Copper Fluxes, kg/wet-season

Fluxes into LSB			Fluxes Out	
Point	700		Past Dumbarton Bridge	6753
Atmospheric	60			
Diffusive	110			
Tributaries	3600			
Bed-Particulate	5873	(calculated)		
Sum	10343			

Flux Balance: $\frac{In - Out}{(In + Out)/2}$ = 0.420

Dissolved Copper Fluxes, kg/wet-season

Fluxes into LSB		Fluxes Out	
Point	560	Past Dumbarton Bridge	628
Atmospheric	0		
Diffusive	110		
Tributaries	360		
Bed-Particulate	0		
Sum	1030		

Flux Balance: $\frac{In - Out}{(In + Out)/2}$ = 0.485

Internal Cycling of Copper to Close Flux Balance: -402

Mass in Sediments, kg

Total Mass	1.90E+06
Background Mass	1.16E+06
Excess (above background)	7.41E+05

Concentration Contributions by Source, ug/L

	Dissolved	Total
C_b	1.6	2.1
C_{point}	0.71	0.89
C_{atm}	0.00	0.08
$C_{diffusive}$	0.14	0.14
$C_{tributaries}$	0.46	4.58
$C_{bed\text{-}particulate}$	0.00	7.48
$C_{cycling\ sum}$	-0.51	

TSSwet= 182.41 **mg/L**

WET SEASON NICKEL CALCULATIONS

INPUT DATA FOR FLUX CALCULATIONS IN LOWER SOUTH SAN FRANCISCO BAY

------------------------ WET SEASON (1 December through 31 May) ------------------------

Water: **Nickel**

Dissolved, ug/L				Total, ug/L				
C_d =	2.9	@ Station	SB02	C_T =	20.6	@ Station	SB02	
C_{db} =	1.6	@ Station	BB30	C_{Tb} =	2.5	@ Station	BB30	(used for calculations)
C_{db} =	2.6	@ Station	BA40/30	C_{Tb} =	5.2	@ Station	BA40/30	(used for reference only)

Sediment Bed: **Nickel**

X_{bed} = 109 mg/kg at station BA21

$X_{background}$ = 90 mg/kg at station NR San Mateo Bridge

T = Thickness for mass calculation = 1 m

ρ = Bulk density = 1400 kg/m^3

External Total Nickel Loadings, kg/wet-season

M_{Point}	800
M_{Trib}	6100
$M_{Diff\ Sed}$	360
M_{Atm}	15
$M_{Particulate\text{-}bed}$	to be calculated

RESULTS - NICKEL (WET SEASON)

----------------- WET SEASON (1 December through 31 May) -------------------

Total Nickel Fluxes, kg/wet-season

Fluxes into LSB			Fluxes Out	
Point	800		Past Dumbarton Bridge	14214
Atmospheric	15			
Diffusive	360			
Tributaries	6100			
Bed-Particulate	15613	(calculated)		
Sum	22888			

Flux Balance: $\dfrac{In - Out}{(In + Out)/2}$ = 0.468

Dissolved Nickel Fluxes, kg/wet-season

Fluxes into LSB		Fluxes Out	
Point	640	Past Dumbarton Bridge	1021
Atmospheric	0		
Diffusive	360		
Tributaries	610		
Bed-Particulate	0		
Sum	1610		

Flux Balance: $\dfrac{In - Out}{(In + Out)/2}$ = 0.448

Internal Cycling of Nickel to Close Flux Balance: -589

Mass in Sediments, kg

Total Mass	5.05E+06
Background Mass	4.17E+06
Excess (above background)	8.80E+05

Concentration Contributions by Source, ug/L

	Dissolved	Total
C_b	1.6	2.5
C_{point}	0.81	1.02
C_{atm}	0.00	0.02
$C_{diffusive}$	0.46	0.46
$C_{tributaries}$	0.78	7.77
$C_{bed\text{-}particulate}$	0.00	19.88
$C_{cycling\ sum}$	-0.75	

TSSwet= 182.41 **mg/L**

SENSITIVITY ANALYSIS
Copper - Dry Season

Perturbed Variable	Bed Particulate Flux			Endpoint Variable		Internal Cycling Dissolved Flux			Endpoint Variable	
		% change in variable		Δ total bed particulate flux			% change in variable		Δ internal cycling dissolved flux	
Δ	Original	+50%	-50%	+50%	-50%	Original	+50%	-50%	+50%	-50%
± 50% C_d	7101	NA	NA	NA	NA	538	1834	-758	241%	-241%
± 50% C_{db}	7101	NA	NA	NA	NA	538	-169	1245	-131%	131%
± 50% C_T	7101	11931	2272	68%	-68%	538	NA	NA	NA	NA
± 50% C_{Tb}	7101	6238	7965	-12%	12%	538	NA	NA	NA	NA
± 50% TSS	7101	7101	7101	0%	0%	538	538	538	0%	0%
± 50% τ	7101	4458	15033	-37%	112%	538	145	1716	-73%	219%
± 50% Point Flux										
dissolved	7101	7101	7101	0%	0%	538	338	738	-37%	37%
total	7101	6851	7351	-4%	4%	538	538	538	0%	0%
± 50% Tributary Flux										
dissolved	7101	7101	7101	0%	0%	538	473	603	-12%	12%
total	7101	7021	7181	-1%	1%	538	538	538	0%	0%
± 50% Diffusive Flux	7101	NA	NA	NA	NA	538	483	593	-10%	10%

SENSITIVITY ANALYSIS
Nickel - Dry Season

Perturbed Variable	Bed Particulate Flux			Endpoint Variable		Internal Cycling Dissolved Flux			Endpoint Variable	
		% change in variable		Δ total bed particulate flux			% change in variable		Δ internal cycling dissolved flux	
Δ	Original	+50%	-50%	+50%	-50%	Original	+50%	-50%	+50%	-50%
± 50% C_d	18027	NA	NA	NA	NA	696	2188	-796	214%	-214%
± 50% C_{db}	18027	NA	NA	NA	NA	696	67	1324	-90%	90%
± 50% C_T	18027	18027	18027	0%	0%	696	NA	NA	NA	NA
± 50% C_{Tb}	18027	18027	18027	0%	0%	696	NA	NA	NA	NA
± 50% TSS	18027	18027	18027	0%	0%	696	696	696	0%	0%
± 50% τ	18027	11315	38160	-37%	112%	696	120	2423	-83%	248%
± 50% Point Flux										
dissolved	18027	18027	18027	0%	0%	696	376	1016	-46%	46%
total	18027	18027	18027	0%	0%	696	696	696	0%	0%
± 50% Tributary Flux										
dissolved	18027	18027	18027	0%	0%	696	680	712	-2%	2%
total	18027	18027	18027	0%	0%	696	696	696	0%	0%
± 50% Diffusive Flux	18027	NA	NA	NA	NA	696	516	876	-26%	26%

SENSITIVITY ANALYSIS
Copper - Wet Season

Perturbed Variable	Bed Particulate Flux			Endpoint Variable		Internal Cycling Dissolved Flux			Endpoint Variable	
		% change in variable		Δ total bed particulate flux			% change in variable		Δ internal cycling dissolved flux	
Δ	Original	+50%	-50%	+50%	-50%	Original	+50%	-50%	+50%	-50%
± 50% C_d	5873	NA	NA	NA	NA	-402	541	-1344	-235%	235%
± 50% C_{db}	5873	NA	NA	NA	NA	-402	-1030	226	156%	-156%
± 50% C_T	5873	5873	5873	0%	0%	-402	NA	NA	NA	NA
± 50% C_{Tb}	5873	5873	5873	0%	0%	-402	NA	NA	NA	NA
± 50% TSS	5873	8809	2936	50%	-50%	-402	-402	-402	0%	0%
± 50% τ	5873	3915	11746	-33%	100%	-402	-402	-402	0%	0%
± 50% Point Flux	5873					-402				
dissolved	5873	5873	5873	0%	0%	-402	-682	-122	70%	-70%
total	5873	5873	5873	0%	0%	-402	-402	-402	0%	0%
± 50% Tributary Flux	5873					-402				
dissolved	5873	5873	5873	0%	0%	-402	-582	-222	45%	-45%
total	5873	5873	5873	0%	0%	-402	-402	-402	0%	0%
± 50% Diffusive Flux	5873	NA	NA	NA	NA	-402	-457	-347	14%	-14%

SENSITIVITY ANALYSIS
Nickel - Wet Season

Perturbed Variable	Bed Particulate Flux			Endpoint Variable		Internal Cycling Dissolved Flux			Endpoint Variable	
		% change in variable		Δ total bed particulate flux			% change in variable		Δ internal cycling dissolved flux	
Δ	Original	+50%	-50%	+50%	-50%	Original	+50%	-50%	+50%	-50%
± 50% C_d	15613	NA	NA	NA	NA	-589	550	-1728	-193%	193%
± 50% C_{db}	15613	NA	NA	NA	NA	-589	-1217	39	107%	-107%
± 50% C_T	15613	15613	15613	0%	0%	-589	NA	NA	NA	NA
± 50% C_{Tb}	15613	15613	15613	0%	0%	-589	NA	NA	NA	NA
± 50% TSS	15613	23420	7807	50%	-50%	-589	-589	-589	0%	0%
± 50% τ	15613	10409	31227	-33%	100%	-589	-589	-589	0%	0%
± 50% Point Flux	15613					-589				
dissolved	15613	15613	15613	0%	0%	-589	-909	-269	54%	-54%
total	15613	15613	15613	0%	0%	-589	-589	-589	0%	0%
± 50% Tributary Flux	15613					-589				
dissolved	15613	15613	15613	0%	0%	-589	-894	-284	52%	-52%
total	15613	15613	15613	0%	0%	-589	-589	-589	0%	0%
± 50% Diffusive Flux	15613	NA	NA	NA	NA	-589	-769	-409	31%	-31%

B.2 Fluxes Between Dissolved and Adsorbed Phases in Water Column for Copper

An approach to calculating fluxes between the adsorbed and dissolved phases of copper in the water column is shown. No such parallel approach for nickel is made, since kinetic data to do so are not currently known. The approach is similar to that used by Wood et al. (1995), and Monismith et al. (1999).

$Flux_{desorb}$	=	$V_{LSB}k_bC_s$	(6)
V_{LSB}	=	volume of water in LSB ($\sim 8 \cdot 6 \cdot 10^7$ m^3 at mean tide)	
k_b	=	$10^{-1.4}$ h^{-1} (Wood et al., 1995)	
C_S	=	(5.2-3.3) µg/L, difference between total and dissolved concentrations	

The adsorbing flux is:

$$Flux_{adsorb} = V_{LSB}k_f \times Cu^{++} \times S \tag{7}$$

$$= V_{LSB}k_f \frac{Cu^{++}}{C_d} C_d S$$

$$= V_{LSB}k_f \alpha C_d S$$

where

$$k_f \approx 10^{0.28} lmg^{-1}h^{-1}$$

$$\alpha = \begin{Bmatrix} .001, & Wood\ et\ al.(1995) \\ .0004, & Monismith\ et\ al.(1999) \\ 0.002\ to\ 0.0048, & this\ report\ (Appendix A) \end{Bmatrix}$$

Consider that at equilibrium

$$\text{Flux}_{\text{desorb}} \approx \text{Flux}_{\text{adsorb}}$$

$$\text{or} \quad K_p = \frac{C_s}{C_d S} = \frac{k_f \alpha}{k_b}$$

Typical values of $K_p \approx 14000$ l/kg, based on observed data, and prior publication (e.g. Wood et al., 1995)

Calculate K_p based on the three estimates of α:

$$Kp\,(\text{l/kg}) = \begin{Bmatrix} 48000\ \ell/\text{kg} \\ 19200\ \ell/\text{kg} \\ 192000\ \ell/\text{kg} \end{Bmatrix}$$

Of these three estimates, $K_p = 19200\ \ell/\text{kg}$ is closer to observed data, so $\alpha = 0.0004$ is used.

By using the data shown in equations (6) and (7) the adsorbing and desorbing fluxes are on the order of 10^4-10^5 kg/yr.

B.3 Calculation of Total Copper and Nickel Concentrations in LSB Due to Point Sources Only

For this calculation, only point source contributions are considered in calculating M and $\dot{M}$. The results pertain to the dry season only.

$$\tau_H = \frac{M}{\dot{M}} = \frac{C_T V}{\dot{M}}$$

$$\text{or } C_T = \frac{\dot{M}}{V} \tau_H$$

$$\dot{M} = 500\,\text{kg/dry-season(Cu) or } 800\,\text{kg/dry-season(Ni)}$$

$$V = 8 \cdot 6 \cdot 10^7\,\text{m}^3$$

$$\tau_H = 20\,\text{days}$$

$$\underline{\text{Copper}}\ C_{T-\text{point}} = \frac{500\,\text{kg/dry-season}}{8 \cdot 6 \cdot 10^7\,\text{m}^3} 20\,\text{days} \times \frac{\text{dry-season}}{\frac{365}{2}\text{days}} \times 10^6\,\text{mg/kg}$$

$$= 0.5\,\mu\text{g/L}$$

$$\underline{\text{Nickel}}\ C_{T-\text{point}} = 0.8\,\mu\text{g/L}$$

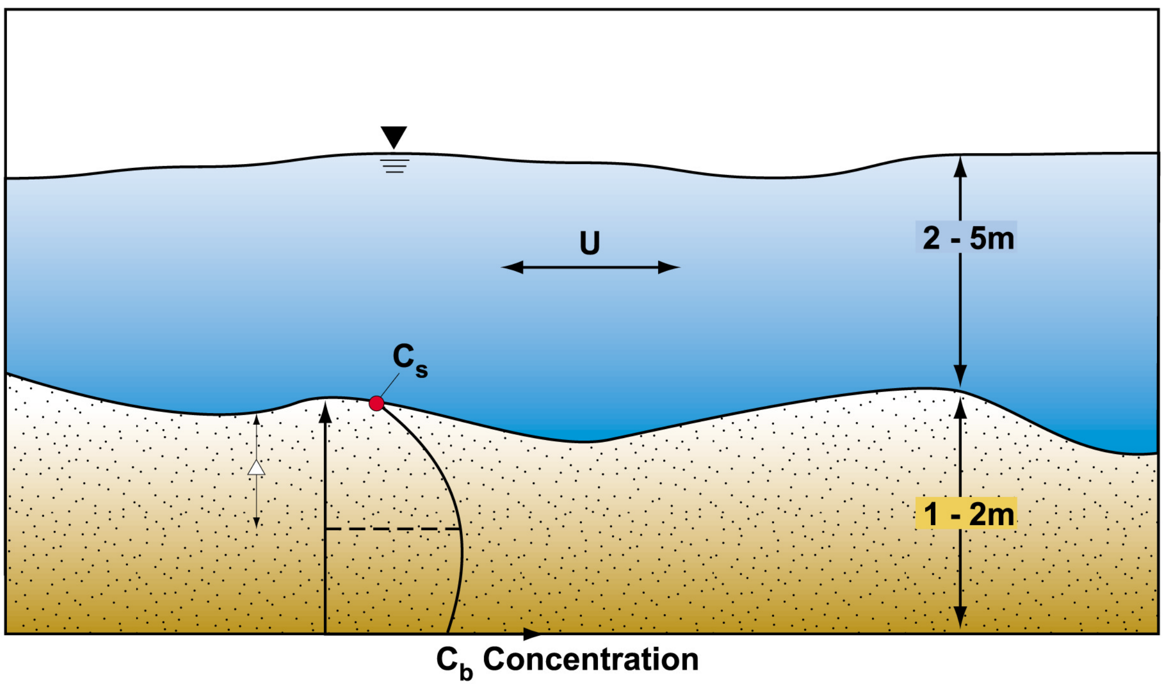
APPENDIX C

APPROXIMATION OF DISSOLVED FLUXES OF COPPER AND NICKEL FROM SEDIMENTS

C.1 Introduction and Assumptions

In this appendix, alternative estimates of dissolved fluxes of copper and nickel are generated using a simplified method, and using data intended to generate order of magnitude, upper limit estimates of the flux.

A sketch of the scenario simulated is shown below. The dissolved metal profile is shown.



The assumptions used to make the estimates are:

- The flux is always assumed to be into the water column
- A steady-state situation is assumed to exist
- The concentration at the sediment water interface (C_s) is negligible relative to the concentration at depth Δ (C_b)
- Precipitation of copper and nickel over depth is neglected
- A diffusion process is the major long-term driving mechanism

C.2 Calculations and Results

Based on these assumptions, the diffusive flux is:

$$F_{diffusive} = \theta_w A_B D_e (C_b - C_{su})/\Delta \tag{1}$$

where

A_B	=	bottom area ($3.3 \bullet 10^7$ m^2)
D_e	=	effective diffusion coefficient ($6 \bullet 10^{-6} cm^2/s$, based on Sañudo-Wilhelmy et al. (1996))
Δ	=	distance over which concentration gradient occurs (Δ = 1 cm, 2 cm, 5 cm assumed range, based on Sañudo-Wilhelmy et al. (1996))
C_b	=	dissolved concentration in bed (C_b = 4.4,10 µg/L assumed for copper; 10, 25 µg/L assumed for nickel based on range of data in Sanudo-Wilhelmy et al. (1996)
θ_w	=	porosity of sediments (0.4 assumed)
C_{su}	=	surface water dissolved concentration (3.2 µg/L for Cu; 3.3 µg/L for Ni)

The range of fluxes is shown below:

Predicted Flux: Copper (kg/yr)		
Δ, cm	C_b = 4.4 µg/L	C_b = 10 µg/L
1	30	170
2	15	84
5	6	33

Predicted Flux: Nickel (kg/yr)		
Δ, cm	C_b = 10 µg/L	C_b = 20 µg/L
1	170	540
2	85	270
5	34	110

The range of copper and nickel fluxes are 6–170 kg/yr and 34–540 kg/yr, respectively. The upper ends of these estimates are similar to those in the Source Characterization Report (URS Greiner Woodward Clyde, 1998).

APPENDIX D

TABLE OF RELATIVE IMPORTANCE OF FACTORS THAT INFLUENCE FATE OF COPPER AND NICKEL IN LOWER SOUTH BAY

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Table D
Relative Importance of Factors that Influence Fate of Copper and Nickel in Lower South Bay

Factor	Relative Importance of Factor	Relative Uncertainty in Quantification of Factor	Potential Short-term Studies to Provide Data and/or to Further Quantify Process Representation	Potential Reduction in Uncertainties
Sources of Copper and Nickel				
• Point	Dry season: low Local impact: moderate Wet season: low Lower South Bay regional effects: low	Low	None	Not applicable
• Watershed to Lower South Bay	Dry season: low Wet season: high Effects: regionally wide	High because complexity of watershed processes	Update loading estimates using best available tools, and most recent data; characterize variability associated with dry, normal, and wet years	Moderate
• Atmospheric deposition	Low	High	None	Not applicable
• Soluble flux from sediment bed	Dry season: low Wet season: low Note: flux acts diffusely over bed to minimize local impacts	High	• Model sensitivity analyses during benchmarking • Review ongoing flux chamber results (to be available in summer 1999) conducted by Moss Landing Marine Labs	Low
• Particulate copper flux from Sediment bed	High	High	May require exploratory modeling during benchmarking; solicit input from expert panel	Low
Physical Processes				
Hydrodynamics				
• Dry season	High	Low	None	Not applicable
• Wet season	High	High	Flushing time estimates for different wet weather conditions	High

Table D
Relative Importance of Factors that Influence Fate of Copper and Nickel in Lower South Bay

Factor	Relative Importance of Factor	Relative Uncertainty in Quantification of Factor	Potential Short-term Studies to Provide Data and/or to Further Quantify Process Representation	Potential Reduction in Uncertainties
• Location of northern boundary of study area	Moderate	High	This issue is best resolved by modeling the effects of choosing different boundary locations and conditions for both dry and wet seasons	Moderate to high
Sediment Transport	High	High	Preliminary sensitivity modeling during benchmarking should be done as a first step; then solicit input from expert panel	Low to moderate
• Boundary conditions at sediment/water interface	High	Moderate	Review, summarize, and use previous work on parameterizing sediment exchange	Low
• Particle size distribution in sediment bed and in water column	Moderate	High	Evaluate particle size distributions at several locations in South Bay, at several depths in the water column, and during dry and wet seasons	Low to moderate
• External sediment loading to South Bay	Moderate	High	Evaluate relative loading from internal and external sources; determine watershed loading that drop out in stream channels, and subsequent resuspension and transport into bay	Low to moderate
Water Temperature	Moderate	Low	None	Not applicable
Forcing Functions				
• Tides	High	Low	None	Not applicable
• Winds	High	Low	None	Not applicable
• Surface water flows, and evaporation	Low to moderate, depending on season of year	Low	None	Not applicable

Table D
Relative Importance of Factors that Influence Fate of Copper and Nickel in Lower South Bay

Factor	Relative Importance of Factor	Relative Uncertainty in Quantification of Factor	Potential Short-term Studies to Provide Data and/or to Further Quantify Process Representation	Potential Reduction in Uncertainties
• Bathymetry	High	Moderate to low	Use most current bathymetric data; likely more recent data are available for parts of the bay	Moderate
Chemical Processes in Water Column				
Speciation				
• Inorganic dissolved	High	Low, using geochemical equilibrium modeling for relative distribution of inorganic species	None	Not applicable
• L1-complexes (strong complexes)	High	High	Determine Cu-L1 complex concentrations in bay waters relative to other species at same time; use expert input to develop kinetic data	Moderate to high
• L2-complexes	Moderate	Moderate	Repeat above	Moderate to high
• Sorption	High	Moderate: vertical distribution of sediments in water column Moderate to high: adsorption/desorption rates, especially for nickel	• Collect trace metal data over depth in water column to determine if vertical concentration gradients exist • Estimate rates of adsorption/desorption under conditions appropriate to South Bay	Moderate
• Colloidal	Low	High	None	Not applicable
• Solubility limits	Low (dissolved phase concentrations appear to be well below solubilities)	moderate	None	Not applicable
• Oxidation-reduction	Low	Low	None	Not applicable
• Competition with other ions for adsorption sites, etc.	Low	Moderate	None	Not applicable

Table D
Relative Importance of Factors that Influence Fate of Copper and Nickel in Lower South Bay

Factor	Relative Importance of Factor	Relative Uncertainty in Quantification of Factor	Potential Short-term Studies to Provide Data and/or to Further Quantify Process Representation	Potential Reduction in Uncertainties
Chemical Processes in Bedded Sediments				
Speciation				
• Dissolved	Low	High, especially over depth within sediments	None, if dissolved flux to water column is unimportant	Not applicable
• Adsorbed	Low	High	Determine adsorption/desorption kinetics appropriate for bedded sediment conditions	Moderate
• Solubility limits	Low	High	None	Not applicable
• Oxidation-reduction	Low	High	None	Not applicable
• Competition with other ions for adsorption/desorption sites, etc.	Low	High	None	Not applicable
Biological Processes				
• Bioavailability	High for uptake and toxicity	Moderate	Model analyses of ligand fate and effects on bioavailability	
• Competition for uptake	Potentially high for uptake and toxicity	High	Algal uptake/toxicity studies with competing metals	Moderate to high
• Accumulation	High for quantifying tissue concentrations and better for estimating phytoplankton effects on cycling	Low for benthic bivalves High for all other organisms	Phytoplankton uptake studies. Field measurements of Cu and Ni in zooplankton and fish of Lower South Bay.	High
• Uptake/elimination kinetics	High for food web modeling or estimating tissue concentrations under different scenarios	Moderate	Literature review of uptake/elimination parameters. Model analyses of food web accumulation.	Moderate

APPENDIX E

SUMMARY OF TRC REVIEW

APPENDIX E

Report to the TMDL Work Group on the Technical Review Committee Review of the Conceptual Model Report for Copper and Nickel in Lower South San Francisco Bay

DRAFT

June 16, 1999

The review of the documents produced in the calculation of total maximum daily loads (TMDLs) for copper and nickel in South San Francisco Bay by a Technical Review Committee (TRC) is an important part of the overall TMDL project plan. The purpose of the TRC review process is to establish a solid technical basis for project activities, to establish and maintain the trust and support of a wide range of interested stakeholders, and to acquire new ideas and perspectives.

The *Draft Final Conceptual Model Report for Copper and Nickel in Lower South San Francisco Bay* (Conceptual Model Report) was the first of the TMDL documents to be reviewed by the Technical Review Committee. The purpose of this report is to provide a record of the technical review process, present the comments of the Technical Review Committee members, to evaluate the effectiveness of this review process, and to identify the actions that are proposed in response to the Technical Review Committee's comments on the Conceptual Model Report.

1. Meeting Summary

A Technical Review Committee (TRC) was convened on April 23, 1999 to review the *Draft Final Conceptual Model Report for Copper and Nickel in Lower South San Francisco Bay* (Tetra Tech, 1999). The members of the TRC were:

- Dr. Janet Hering, California Institute of Technology
- Dr. Sam Luoma, U.S. Geological Survey
- Dr. Stephen Monismith, Stanford University

Resumes for the TRC members are presented in the TMDL Task 9 TRC procedures document (Tetra Tech, 1998). The process of selecting the TRC members is also described in the Task 9 report.

Two weeks prior to the April 23 meeting the TRC members were provided with the Conceptual Model Report and a list of questions that should be considered in their review. The information presented to the TRC prior to the meeting is included in Attachment 1. The reviewers were also provided with a brief overview of the TMDL efforts underway (Attachment 2) and a copy of the TRC Procedures Document (Tetra Tech, 1998).

There were three parts to the review meeting. The first part consisted of a presentation by the authors of the Conceptual Model Report. This presentation lead to several questions, and the graphics that were prepared for the meeting were used several times to guide the discussions. In the second part of the meeting the reviewers met to compare notes and to discuss their findings. A question and answer session made up the third part of the meeting. The reviewers provided answers to the questions that were developed to guide the review, and the reviewers asked several questions regarding information presented in the Conceptual Model Report.

2. Summary of Findings

The written comments provided by the TRC members are presented in Attachment 3. The following is a summary of these findings. First, the general findings on the ability of the Conceptual Model Report to meet the overall objectives are presented. Next, the specific findings from the written comments of the reviewers are summarized. The primary objective of this portion of the summary is to confirm that the most important features of the reviewer's comments have been captured. (*This summary was also presented to the reviewers to make sure that this objective was met, and their responses are provided in Attachment 4*.) The preparation of this summary also provides a basis for identifying the required responses and modifications to the Conceptual Model Report.

2.1 General Findings of the TRC

The reviewers found the report provided a good generic framework and synthesis of the model elements. The reviewers found that the presentation of information was clear, easily followed, and that the graphics did a good job of communicating the information. Although the reviewers found that the Conceptual Model Report provided a good summary of the existing information, all three reviewers identified issues that they felt were not adequately addressed.

2.2 Specific Findings of the TRC

The reviewers made detailed comments in five primary areas:

1. Use of Existing Data in the Conceptual
2. Model Uncertainties Associated with Copper and Nickel Loading Estimates
3. Bioavailability, Toxicity, and Trophic Transfer of Copper and Nickel
4. Uncertainties in the Conceptual Model
5. Recommendations for Additional Studies

The comments of the reviewers in each of these five areas are summarized below.

2.2.1 Representation of the Existing Data in the Conceptual Model

Three related issues were identified. The first was the need to provide more detailed referencing of the data and concepts presented in the report. It was noted that while some of the data presented were obtained from the peer reviewed literature while other data were from calculations presented in unpublished reports and conference presentations. The second issue was raised in a related discussion during the review meeting. It was noted that the report focuses almost exclusively on average concentrations. The need to present ranges of values in calculations presented was identified. The presentation of average values in the mass balance model understates the uncertainty that exists in these estimates. The tendency to summarize information in this manner is evident in the Executive Summary of the report, which understates the uncertainty associated with the existing knowledge. The third issue is also related to the use of average values. The reviewers noted that there is a need to present the differences that exist due to seasonality and/or seasonal cycles.

2.2.2 Uncertainties Associated with Copper and Nickel Loading Estimates

A section of the Conceptual Model Report is dedicated to summarizing the existing knowledge regarding copper and nickel loadings to Lower South San Francisco Bay and to estimating mass balances. There was a consensus among the reviewers that "the report does not adequately address the uncertainties regarding loadings, which are significant". One of the key areas of uncertainty was the sediment flux calculations in general and the copper loading due to resuspension in particular. A clear recommendation was made to provide a more detailed description of how the flux from sediments was estimated for both copper and nickel. The reviewers also pointed out other specific instances where there is a need to present information on the uncertainties associated with loading estimates. These include the need to provide more detailed information on the methods used in these analyses, the need to recognize that no good data exist that allow us to describe anthropogenically derived loadings from local tributaries, and the need to describe the effects of seasonality and/or seasonal cycles.

2.2.3 Bioavailability, Toxicity, and Trophic Transfer of Copper and Nickel

The reviewers identified several issues related to bioavailability, toxicity, and trophic transfer. The discussions ranged from kinetic and thermodynamic controls on bioavailability, to the potential for uptake of copper and nickel at the cellular level, to the concern that higher trophic levels and toxicity issues were not adequately addressed. The need to address the potential effects of ambient concentrations of copper and nickel on phytoplankton, an issue previously raised by Ken Bruland at the TMDL Indicator Workshop, was identified. Bioavailability and dietary uptake to consumer organisms, possible toxic effects on phytoplankton and consumer community composition, and metal release during remineralization of phytoplankton in the water and sediments were also identified.

2.2.4 Uncertainties in the Conceptual Model

A general conclusion of the reviewers was that there are numerous uncertainties associated with the conceptual model and that there are several important uncertainties that were not listed in the report. The primary uncertainties, including those identified above, are:

1. Flux calculations
    - Better estimates are needed regarding adsorption and desorption rate constants used to estimate sediment fluxes.
    - Better estimates are needed for the mass exchanges between Lower South San Francisco Bay and the Central Bay. Consideration should be given to differentiating between dry and wet seasons.
    - More detailed information is needed to describe anthropogenically derived loadings from local tributaries.

2. Sediment accumulation
    - More information is needed regarding sediment dynamics including the analysis of long-term bathymetric changes and geochemical analysis of sediment cores.
    - Determination of the recovery time in this system after sediments have been contaminated.

3. Bioavailability
    - Little direct information is available on the uptake, accumulation and toxicity of copper and nickel to phytoplankton under specific water quality and speciation conditions in Lower South San Francisco Bay.
    - Nickel cycling , bioavailability, and toxicity are big areas of uncertainty.

2.2.5 Recommendations for Additional Studies

Several recommendations were made for additional studies. These ranged from studies that would be important for establishing the TMDL, to studies that would improve the conceptual model. These include:

1. Tributary loads should be monitored directly in representative streams and years.

2. Adsorption and desorption rates from suspended sediment particles need to be studied, including particle size effects on these rates.

3. Sediment accumulation and release fluxes should be studied through analysis of historical bathymetric changes and geochemical studies of sediment cores. Seasonal variations in accumulation and release should be studied, as well as the recovery time after periods of contamination.

4. The effects of wind wave resuspension of sediments in the shoals versus resuspension by tidal currents in the channels needs to be evaluated, as well as sediment rheology parameters that influence erosion and resuspension.

5. The release of metals from decomposition of phytoplankton in the sediments should be studied.

6. Transport processes during wet weather periods need to be studied.

7. A dynamic conceptual model should be developed that includes seasonal and event-driven variations and more site-specific details for the Lower South Bay.

8. The effects of colloidal metals and their bioavailability to filter-feeders should be evaluated.

9. There is a need to begin to study the factors controlling the fate, bioavailability and effects of nickel. One of the biggest questions is how to natural inputs influence effects, as compared to inputs from urban runoff and POTWs.

3. Questions Presented to the TRC Reviewers to Guide the Meeting

During the afternoon session of the review meeting the questions that were presented to the TRC members prior to the meeting were discussed. One of the reviewers (J. Hering, Appendix 3) also submitted written responses to these questions. The responses to these questions are presented followed by an evaluation of their effectiveness in helping to guide the review process.

3.1 Four Questions from the Co-Chairmen of the TMDL Work Group

Four basic questions were sent out to the reviewers with the Conceptual Model Report. The purpose of these questions was to help focus the review process.

3.1.1 Question 1. The first step in identifying the most important processes was to develop estimates of loadings, mass balances, and inventories of copper and nickel in the Lower South San Francisco Bay. Is the approach that was used to develop these estimates valid and are the reported mass balances credible?

One of the concerns expressed was that the information used to develop the loadings was obtained from the TMDL Source Characterization Report (URS Greiner Woodward Clyde and Tetra Tech, 1999) which was unavailable to the reviewers. There was also a general concern expressed regarding the adequacy of the description of the methods used to estimate the flux from the sediments. Finally, the need to represent the range of values and the uncertainties associated with the chemical inventory and loading diagrams was identified.

3.1.2 Question 2. The conceptual model has four major components (loadings, sediment transport, copper and nickel cycling, and forcing functions). Has the technical information on each of these areas been adequately summarized?

In general the reviewers found that the summary provided was adequate, but that there were instances where the summarized information may be misleading to the non-expert reader.

3.1.3 Question 3. The conceptual model was developed as a communication tool. Are the graphics and the descriptions effective in communicating the technical information?

Positive feedback was received on the figures and graphics. It was found that they were helpful in presenting the necessary information.

3.1.4 Question 4. Chapter 7 summarizes the existing information and identifies existing uncertainties. Short-term studies have also been identified to address these uncertainties. Have the major uncertainties been identified and are the studies that have been identified appropriate?

The studies described in Chapter 7 coincide with many of the uncertainties that were identified by the reviewers. Nevertheless, the reviewers stated that there are more uncertainties that were not listed. Most of the additional uncertainties identified are summarized in Section 2.2.

3.2 Additional Review Questions

Additional questions were prepared by members of the TMDL Work Group's Subcommittee for the TRC Review.

3.2.1 In the conceptual model shown in Figure 2-3, the estimate of adsorption of copper onto suspended sediment is 82% of the estimate of desorption of copper. Given the uncertainties in each of these estimates, is it reasonable to conclude that they are significantly different? In other words, how certain are we of the magnitude or direction of the contribution of resuspension to dissolved copper concentrations? Are there field data that support (or contradict) the idea that resuspension contributes to dissolved concentrations of copper?

This question received a lot of attention in the morning discussion session. The adsorption/desorption and contribution of resuspension of copper fluxes are highly uncertain. This part of the conceptual model needs to be much more constrained. This is also one of the areas identified in Section 7 of the report as requiring additional study.

3.2.2 Figures 2-3 and 2-5 show net flux of copper and nickel past the Dumbarton. However, the calculation of net nickel flux in Appendix B.1 does not take into account nickel concentrations north of the Dumbarton, in the water which will replace the exported south-of-Dumbarton water. How should copper and nickel fluxes from north of Dumbarton be treated in the mass-balance estimates of the conceptual model?

Cu and Ni concentrations north of Dumbarton are lower (but not negligible) compared to LSB waters. The closest north-of-Dumbarton station exhibits elevated metal concentrations, possibly an indicator of LSB influence. It would be interesting to see how dissolved Cu concentrations plot against salinity; this might indicate Cu sources or sinks within LSB and/or north-of-Dumbarton. Note also that the solute flushing time, T_f, is valid only for dry season conditions; it is not clear how (or whether) a comparable calculation was made for wet season conditions.

Stephen Monismith in his written responses (Attachment 3) also addressed this issue.

3.2.3 Will the conceptual model help us conduct computer modeling and calculate the TMDL? In Dr. Hering's written response she stated that it was not her sense from the report that the conceptual model could be directly applied in a computer model to calculated TMDLs. She stated that "I would not judge it to be sufficient for this purpose". This issue is addressed further in Section 4.

3.3 Evaluation of Questions and Recommendations for Future TRC Meetings

It was anticipated that these questions would guide the review process and help to focus the discussions of the TRC meeting. However, this was not the case. The discussions focused more on the details of the Conceptual Model Report and the uncertainties that exist. Although the members of the TMDL Work Group members that attended the meeting agreed that TRC meeting was successful in meeting the overall objectives, there was also agreement that the process could be improved.

The reviewers thought that the review process could be improved by focusing the discussion at the TRC meeting on specific issues. The Conceptual Model Report, for example, contains an extremely large amount of information. In the TRC meeting the discussions focused on a large number of specific issues that were of particular interest to the technical experts. The questions that are submitted to the TRC members should more closely coincide with the objectives of the review process.

There was also agreement that conference calls in combination with some written communication between the TRC members and the TMDL Work Group would be helpful. The purpose of this call would be to discuss the objectives, agenda, and expectations of the TMDL Work Group. The TMDL Work Group should also request the TRC to comment (in writing) on their perceptions of the main strengths and weaknesses of the report and to identify questions. The meeting would then be structured more closely around the questions and would be more closely facilitated to make sure these questions are addressed.

4. Preparation of the Final Conceptual Model Report

The authors of the Conceptual Model Report agree with the overall comments of the TRC members. There are numerous uncertainties that need to be identified, and there are specific changes to the report that would help the role of the document as a resource for the TMDL project. However, there are limits to a conceptual model. To resolve many of the uncertainties that exist, additional data need to be collected. To provide a more thorough analysis of copper and nickel fluxes within the system, more detailed, computer-based modeling efforts are required.

Base on the review comments, four major changes to the Conceptual Model Report are proposed:

1. Incorporation of Technical Review Comments.

   The reviewers have not only provided an excellent review of the document, they have provided many additional ideas and perspectives. Their review comments as well as this summary report will be included as an appendix to the Conceptual Model Report. The introduction to the Conceptual Model Report will be modified to acknowledge the reviewer's contributions and to direct the reader to the reviewer's comments.

2. Changes to the chemical concentration, inventories and loading figures (Figures 2-2 through 2-5).

   These figures summarize a great deal of the information that is presented in the conceptual model. These figures will be modified in three ways. First, the existing figures will be modified to show, where possible, the range of values for ambient concentrations and fluxes. Second, these figures will also be modified to represent the uncertainty that is associated with the estimated magnitude of the different sources of copper and nickel in the system. For example, the representation of the estimated fluxes of copper and nickel from the sediments and tributaries will be modified to convey the fact that, given the existing uncertainties, these are the two most important sources and that they should receive equal attention in future efforts to understand copper and nickel sources. Third, a separate set of figures will be produced for wet- and dry-season concentrations and fluxes. A new time-series plot will also be included to show the effects of freshwater flow on copper and nickel concentrations. The goal of these modifications to the figures will be to adequately capture the uncertainties so that they can stand alone and capture the essential information and level of associated uncertainties.

3. Uncertainties

   Numerous uncertainties were identified during the review process. Many of these uncertainties and the TRC more general comments are closely related to the four key areas that were identified in the Draft Final Report: 1) Biogeochemical processes influencing speciation, 2) Effects of speciation and competing metals on phytoplankton uptake and toxicity, 3) Resuspension fluxes and other sediment-water interactions, 4) Wet season tributary loads. The discussions for each of these four areas will be expanded in the Final Conceptual Model Report to incorporate the reviewers comments and the identified uncertainties.

   In the draft document, many uncertainties identified but many of these were deleted in response to the comments that were received from TWG members. A separate section will be added to Chapter 7 to present the identified uncertainties.

4. Technical Appendices

   The technical appendices that describe copper and nickel flux calculations will be expanded to include the information necessary to reproduce the results presented in the Conceptual Model Report.

5. References

Tetra Tech, 1998. Task 9 – Technical Review. Technical Review Committee Procedures Document. Draft Report. September 21, 1998.

URS Greiner Woodward Clyde and Tetra Tech, 1998. Task 2.1 Source Characterization Report. Draft Report. December 1998.

TMDL Work Group Memorandum

FROM: **Tom Mumley and Rainer Hoenicke, Co-Chairmen TMDL Work Group**

TO: **Janet Hering, Sam Luoma, Stephen Monismith**

DATE: **April 13, 1999**

SUBJECT: **Review of Conceptual Model Report for Copper and Nickel in Lower South San Francisco Bay**

Thank you for participating in the review of the enclosed conceptual model report. The conceptual model has been developed as part of the Total Maximum Daily Load (TMDL) project for Lower South San Francisco Bay. The conceptual model report is a companion document to other products that either have been developed (e.g., Source Characterization Report) or will be developed (e.g., the Impairment Assessment Report and the Model Evaluation Report). This report is intended to describe the current understanding of the processes that influence copper and nickel in the Lower South San Francisco Bay. In the introduction to the report, three roles for the conceptual model are described: data synthesis, communication, and project planning.

One of the goals of calculating a TMDL for copper and nickel in Lower South San Francisco Bay is to establish a sound technical basis for municipal wastewater and stormwater permit requirements. The role of the Technical Review Committee is to provide a technical review of the products that will lead to the development of the TMDL.

There are four primary areas that should be considered in your review:

1. The conceptual model describes the current understanding of the processes that influence copper and nickel cycling and that influence toxicity to aquatic organisms. The first step in identifying the most important processes was to develop estimates of loadings, mass balance and inventories of copper and nickel in the Lower South San Francisco Bay.

    - Question 1. *Is the approach that was used to develop these estimates valid and are the reported mass balances credible?*

2. The conceptual model has four major components (loadings, sediment transport, copper and nickel cycling, and forcing functions).

    - Question 2. *Has the technical information on each of these areas been adequately summarized?*

3. The conceptual model was developed as a communication tool.

    - Question 3. *Are the graphics and the descriptions effective in communication the technical information?*

4. Chapter 7 summarizes the existing information and identifies existing uncertainties. Short-term studies have also been identified to address these uncertainties.

    - Question 4. *Have the major uncertainties been identified and are the studies that have been identified appropriate?*

We look forward to meeting with you on April 23 and to receiving your comments on your review of the document. Please contact either of us if you have any questions regarding this review process.

Tom Mumley
California Regional Water Quality Control Board
(510) 622-2395
tem@rb2.swrcb.ca.gov

Rainer Hoenicke
San Francisco Estuary Institute
(510) 231-5731
rainer@sfei.org

Calculation of TMDLs for Copper and Nickel in South San Francisco Bay

Tom Grieb, Tetra Tech, Inc.
Adam Olivieri, EOA, Inc.

The emergence of the TMDL process as an important planning and regulatory decision-making tool is a recent development in national, regional, and local efforts to achieve continued improvement in the quality of the nation's surface waters. The TMDL, or total maximum daily load, establishes the allowable loadings of a pollutant that a water body can receive without violating applicable water quality standards or harming beneficial uses. Although identified in Section 303(d) of the federal Clean Water Act (CWA) over 20 years ago, it is only since 1996 that the TMDL has become an important process for developing state water quality standards.

The development of TMDLs for copper and nickel is required because South San Francisco Bay (South Bay) has been designated an impaired water body under Section 303(d) of the CWA. Although this is a requirement, there is also optimism that these TMDLs will provide a unique opportunity to address the many complex issues associated with setting water quality standards for the South Bay. Stefan Lorenzato, the TMDL coordinator at the State Water Resources Control Board, notes that the collaborative approach that is being taken to prepare these TMDLs is likely to be more successful than the programmatic approach that has traditionally been used by state and local regulatory agencies.

These copper and nickel TMDLs are noteworthy for several reasons. Foremost among them is the fact that they are being independently funded by the City of San Jose. David Tucker and Dan Bruinsma, the City of San Jose's co-project managers, note that "*This is one of the most comprehensive, chemical-specific, environmental assessments ever conducted in San Francisco Bay; a total of $3.5 million has been allocated by the City for this 4-year effort.*" The copper and nickel TMDLs are also being integrated into the ongoing Santa Clara Basin Watershed Management Initiative (WMI), and a major emphasis is being placed on establishing and maintaining public and industry involvement. One indication of the collaborative aspect of this effort, referred to above by Stefan Lorenzato, is the formation of a TMDL Work Group (TWG). The TWG is made up of stakeholders from wastewater and stormwater dischargers, environmental groups, industry, regulatory agencies, and other involved citizens, and it has been formed as part of the WMI's Bay Modeling and Monitoring Subgroup. The charter of this group is to guide the TMDL process and to develop new and preferred ways to make the process understandable and equitable. A Technical Review Committee (TRC) has also been formed to review the technical products of the TMDL effort. The TRC is made up of nationally recognized technical experts in such areas as the behavior of metals in aquatic systems, hydrodynamics, estuarine modeling, ecological effects of trace metals, sediment transport processes, and atmospheric modeling.

The focus of the copper and nickel TMDL efforts during the first year of activity has been in the following five primary areas of investigation:

Data Collection and Analysis. One of the first efforts has been to create an extensive database that is available to both technical and stakeholder personnel involved in the project. The database is unique in that it brings together different types and large volumes of information (over 1.5 million records have been entered so far) focused on the specific issues of TMDL development for copper and nickel in the Lower South San Francisco Bay. Many investigators in the area have contributed to the development of a database that consists of water quality data, sediment quality data, sediment core data, point and nonpoint source loading data, basemap information, bathymetric data, hydrodynamic data, suspended solids data, air quality data, and photographic/satellite imagery.

Additional data will continually be entered, as they become available during the project. To facilitate use and understanding of the data, the database has been created in a Geographic Information System (GIS).

Conceptual Model Development. A conceptual model that depicts the current understanding of the processes that influence copper and nickel cycling in Lower South San Francisco Bay and adjacent Bay waters was recently produced. To communicate the information that has been developed on loadings, sediment transport and copper and nickel cycling, the conceptual model makes extensive use of graphics. The objective of this effort was to develop a tool for effectively communicating the existing information to a wide audience of interested stakeholders. Diagrams such as the one shown in the accompanying figure can be used to facilitate the discussions of upcoming TMDL issues such as source characterization, beneficial-use impairment, simulation model development, and the design of special studies. The conceptual model was the topic of one of the poster sessions at the recent State of the Estuary Conference.

Source Characterization. The major sources of copper and nickel that enter the South Bay are being quantified. The loadings have been divided into four major source categories: wastewater discharges, tributary loads, atmospheric deposition to the surface water, and sediment exchange with the water column within the Bay. This effort is the first step in identifying the major contributors of copper and nickel loading so that appropriate control measures can be developed if necessary. It is also the purpose of this work to identify limitations and uncertainties in the existing loading data so that additional efforts to improve these estimates can be focused in the appropriate areas.

Assessment of Beneficial Use Impairment. In January of this year, over 50 individuals from local regulatory agencies, municipal dischargers, stormwater management groups, environmental groups, and other South Bay stakeholder groups participated in an impairment assessment workshop held at the San Francisco Bay Regional Water Quality Control Board. Information was presented on progress made in developing indicators for assessing impairment to beneficial uses. The results of the workshop were also presented at the recent State of the Estuary Conference. Later this spring, an Impairment Assessment Report will be completed. The purpose of the impairment assessment is to determine if and when and how the beneficial uses of the South Bay are adversely affected by copper and nickel, and what concentrations cause these problems. The results of this assessment will determine the course of all further activities associated with these TMDLs.

Simulation Model Development. The first of several technical reports that will be produced in the evaluation of existing two- and three-dimensional numerical simulation models was completed in December 1998. This document identifies models that could be used in the calculation of TMDLs for copper and nickel in South San Francisco Bay. This evaluation process is important because numerical models will be the primary tool used to evaluate the responses of the South Bay to copper and nickel loading. This initial report identifies the model components that are necessary to simulate and predict the transport and fate of copper and nickel in South San Francisco Bay. Twenty potentially applicable models were identified and classified according to type and functionality, and a subset of 10 models was recommended for further evaluation.

Comments on the TMDL Process

Numerous individuals in the copper and nickel TWG have already made significant time commitments to this process. Tom Mumley of the California Regional Water Quality Control Board and the TWG's co-chairman suggests that "*This is because many people recognize that the up-front involvement of the stakeholders and the level of funding available offers a unique opportunity to achieve resolution of issues that are acknowledged to be both politically contentious and technically complex*." Rainer Hoenicke, the other TWG co-chairman and the program manager for the Regional Monitoring Program for Trace Substances, also points out that *"The information synthesis effort that is part of the problem characterization is particularly relevant, because for most of the stakeholders, this is an invaluable opportunity to become educated about the complex issues surrounding these two metals."* Also, as the program manager for the Regional Monitoring Program for Trace Substances, he is personally excited about the TMDL effort because it demonstrates that the monitoring activities conducted in the estuary will have an impact on environmental decision-making. He is also hopeful that the conceptual model and the other problem definition efforts of the TMDL will help to focus future data collection efforts. Michael Stanley-Jones of the Silicon Valley Toxics Coalition and CLEAN South Bay's environmental coordinator for the Copper-Nickel TMDL has expressed optimism that the tools that are being developed for these TMDLs will provide a strong technical foundation for future TMDL efforts in the San Francisco Bay/Estuary.

Written Comments from the Technical Review Committee Members

1. Comments from Dr. Janet Hering

CONCEPTUAL MODEL REPORT FOR Cu AND Ni IN LOWER SOUTH SAN FRANCISCO BAY: REVIEW

Summary

The Report describes a conceptual model for Cu and Ni in Lower South San Francisco Bay (LSB). The stated goal of the Report is to "provide a technical basis for TMDL project planning" and "to guide the scope and direction of the other tasks, as well as the overall technical approach for the development of the TMDLs."

The Report summarizes loadings, mass balances, and inventories of Cu and Ni in LSB; the estimates of loadings are based on a Source Characterization Report (URS Greiner Woodward Clyde, 1998) which was not available to the TRC. The report then discusses processes thought to dominate the cycling of Cu and Ni in LSB and issues related to the uptake and toxicity of Cu and Ni primarily to phytoplankton (as the most sensitive target organisms).

The Report makes several recommendations regarding future studies, identifying the following four key areas: (1) biogeochemical processes influencing chemical speciation, (2) effects of speciation and competing metals on phytoplankton uptake and toxicity, (3) resuspension fluxes and other sediment-water interactions, and (4) wet season tributary loads.

Comments

The Report makes a very clear and generally insightful presentation of the biogeochemical processes involved in cycling of Cu and Ni in LSB. The logic of the presentation can be easily followed and the graphics are clear and understandable. The Report makes a laudable attempt to develop a model of Cu and Ni cycling that would be simple enough for quantitative application yet does not belie the complexity of the actual system. There are, however, several issues that are not adequately addressed by the Report.

1. <u>Uncertainties regarding loadings</u>. The Report does not adequately address the uncertainties regarding loadings, which are significant. The particulate flux from bed sediments is a <u>key</u> parameter in the conceptual model and it is extremely poorly constrained. The Report does not adequately describe the manner in which this flux was estimated for Cu and does not clearly distinguish between the estimation methods for Cu and Ni. It is striking that the estimated flux is lower for Ni (5,000 kg/y) than for Cu (8,000 kg/y) even though the sediment concentrations are higher for Ni (92 mg/kg) than for Cu (42 mg/kg). Also, this argument seems to rely heavily on adsorption and desorption rate constants derived from Wood et al. (1995). However, this paper addresses <u>diagnostic</u> modeling; the authors state "We have not addressed possible sources of variability in K_d^a other than adsorption kinetics. Probably the most notable of these is the amount of variation in the nature of the suspended particles themselves…" It is not appropriate to use the rate constants from this paper out of context in this fashion. An important question regards the extent and rate of sediment accumulation in LSB. Does the metal content of the sediment reflect historical inputs that may be gradually released back to the overlying water column? How does metal accumulation into and release from sediments vary seasonally?

2. Bioavailability and speciation. The Report relies heavily on the work of Donat et al. (1994) but fails to address a significant finding of that paper. The free cupric ion concentration [Cu^{2+}] calculated for LSB based on several complementary analytical techniques is 0.2 nM ($10^{-9.7}$ M). This value is well within the range of known toxicity to many phytoplankton species (Brand et al., 1986). The corresponding value for [Ni^{2+}] is 22 nM ($10^{-7.7}$ M). Because of the lack of studies of nickel toxicity, it is not clear what effect these concentrations would have on sensitive algal populations. Nonetheless, it is a significant point that these values both for Cu and Ni are high for natural waters. The Report does not define the term bioavailability and the meaning implicit in the Report is somewhat misleading in its confusion of kinetic and thermodynamic controls on bioavailability. There are several key concepts that should be clarified. (i) In general, metals present as strong organic complexes are not bioavailable in that the intact complex is not directly taken up by the cell. (There are two important exceptions to this, Fe(III)-siderophore complexes for which specific cellular uptake mechanisms exist and lipophilic complexes that can passively diffuse through cell membranes.) (ii) When the metal-organic complex is not bioavailable (i.e., the intact complex is not directly taken up by the cell), metal bioavailability (as determined by metal uptake rates and/or the effects of metals on growth rate, motility, etc.) is generally found to be a function of the free metal ion activity or concentration (note that these can be used interchangeably only at fixed ionic strength). This dependence can reflect either thermodynamic or kinetic control (Morel and Hering, 1993). (iii) However, this dependence does not imply that the metal taken up by the cell cannot have initially been present in complexed form. It would be of interest to examine whether, for example, phytoplankton uptake of Ni in EDTA-buffered systems is indeed kinetically limited by the rate of dissociation of the NiEDTA complex. If this were the case, then at steady-state, the Ni uptake rate would be a function of [NiEDTA] rather than [Ni^{2+}] (Morel and Hering, 1993).

3. Potential importance of colloidal species. Donat et al. (1994) specifically note that the metals in their samples are “operationally defined” as dissolved (filtration through 0.45 µm in-line cartridge filter) and could include a colloidal metal fraction. Colloidal metals are excluded from consideration in the Report based on the work of Sañudo-Wilhelmy et al. (1996). This study, however, was performed in January. The colloidal fraction would be expected to be most significant at times of high wind-speed and high suspended sediment concentrations (i.e., summer rather than winter in LSB). The issue of colloidal metals should receive greater attention, particularly with regard to their bioavailability to filter-feeding organisms.

4. Seasonality and temporal variability. The Report focuses almost exclusively on average loadings and/or concentrations. Temporal variability is not addressed except for some distinction made between wet and dry seasons. Metal concentrations in LSB exhibit distinct seasonality; these data are not included in the Report nor are their significance noted. It is unlikely that consideration of annual average loadings and/or concentrations will be sufficient either to understand the cycling of metals in LSB or to assess compliance with short-term (several hours to days) water quality criteria.

5. Role of phytoplankton in metal cycling. Phytoplankton uptake is estimated to be on the order of 1600 kg/yr for Cu and 1900 kg/yr for Ni. However, phytoplankton uptake is not a

permanent sink for metals. Remineralization (and concomitant metal release) is expected both within the water column and at the sediment-water interface. Furthermore, grazing of phytoplankton by benthic organisms has been proposed to control phytoplankton population densities; this extent of grazing could substantially affect metal transfer to higher trophic levels. The possible role of phytoplankton uptake in cycling metals between the water column and sediments requires additional attention.

Responses to TMDL questions

Question 1. No. This question cannot be answered in a satisfactory manner based on the information provided in the Report. The estimates of loadings rely entirely on information unavailable to the TRC. The mass balances are, in key instances, closed by difference and are not sufficiently constrained.

Question 2. In general, the summary provided is adequate but there are some instances where the summarized information may be misleading to the non-expert reader.

Questions 3. Yes.

Question 4. No. In my opinion, the sediment flux issue is crucial and received insufficient attention.

Question A. It was not my sense from the Report that the conceptual model could be directly applied in a computer model to calculate TMDLs. I would not judge it to be sufficient for this purpose.

Question B. The adsorption/desorption and contribution of resuspension to Cu fluxes are highly uncertain. This part of the conceptual model needs to be much more constrained. Some field work on metals in sediments in Massachusetts Bay may be relevant to this question but I have not reviewed this literature recently.

Question C. Cu and Ni concentrations north of Dumbarton are lower (but not negligible) compared to LSB waters. The closest north-of-Dumbarton station exhibits elevated metal concentrations, possibly an indicator of LSB influence. It would be interesting to see how dissolved Cu concentrations plot against salinity; this might indicate Cu sources or sinks within LSB and/or north-of-Dumbarton. Note also that the solute flushing time, T_f, is valid only for dry season conditions; it is not clear how (or whether) a comparable calculation was made for wet season conditions.

Supplemental References

Brand, L.E., Sunda, W.G., Guillard, R.R.L. (1986) Reduction of marine phytoplankton reproduction rates by copper and cadmium. *J. Exp. Mar. Biol. Ecol*., 96: 225-250.

Morel., F.M.M. and Hering, J.G. (1993) *Principles and Applications of Aquatic Chemistry*, Wiley-Interscience, New York, chapter 6.

2. Comments from Dr. Sam Luoma

Sam Luoma's Comments

To: Tom.Griebe@tetratech.com
cc: jhering@its.caltech.edu, monismit@cive.Stanford.EDU, Samuel N Luoma/WRD/USGS/DOI

Subject: Comments on South Bay Conceptual Model

Tom,
The following are a few comments from today's meeting.

1. The South Bay TMDL is highly dependent upon reliable data to describe loadings, and specifically, anthropogenically derived loadings, from the local tributaries. Stream gaging, daily sediment loads, total and dissolved metal concentrations and metal concentrations directly on suspended particulate materials must be determined for at least representative streams in representative years. Eventually every stream should be gaged. This is expensive, but it can be done and it defines what a TMDL is. Literally no good data exists that allow us to derive loads from human activities...that must be clearly stated in the model report.

2. The conceptual model provides a good generic framework to start thinking about what determines metal concentrations, but it lacks important details specific to South Bay. Without such detail I do not believe the model provides an adequate basis for determining the sources and loadings. We can make informed speculation about processes that determine sediment dynamics, seasonal sediment fluxes, phytoplankton blooms and their influence on bioavailability to consumers, seasonal inputs of sediments from North Bay, etc. The next step should be a dynamic conceptual model for some of these critical processes that includes consideration of important system-specific characteristics. It would be very useful to have a list of some of the hypothesis that could explain certain system-specific characteristics. Why do dissolve Cu concentrations fluctuate seasonally? Is the flux out of sediments a) release of historic contamination, b) seasonal input of terrigenously contaminated sediments then gradual desorption through the low flow season, c) seasonal transformation of metals by phytoplankton during the bloom then release of those metals as the organic matter is metabolized during the low flow period? How important are inflows from North Bay (seasonal) in flushing accumulated pollutants out of South Bay? Again, this is not irrelevant detail. The whole system may be run by events or seasonal deviations from annual means. Creative solutions could come from understanding such detail.

3. Nickel and copper are treated equally in the model. However, one of the greatest areas of uncertainty is our poor knowledge of Nickel cycling, inputs from naturally enriched geology and bioavailability. This needs to be emphasized, and listed as a big area of uncertainty. Nickel is a possible cause of the widespread toxicity found in Bay sediments. Shouldn't we know more about its basic behavior, sediment-solution exchange, bioavailability and effects??

4. The model is sadly lacking with regard to biology. As such it is unlikely that it will provide an adequate basis for decisions that will be protective of the Bay ecosystem. The Bruland hypothesis about copper effects on South Bay phytoplankton is not presented. No information is presented on consumer organisms and the effects on these species that have occurred in the past as a result of Cu and/or Ag contamination. No consideration of the make-up the phytoplankton community (e.g. dinoflagellates are missing) or the make-up of the consumer community is presented. No consideration of bioavailability to consumers is presented. Dietary exposure of conumer organisms is ignored in many statements that assume only dissolved Cu and Ni are important. Today's regulatory standards allow local entities to continue this dated thinking, but that will change in the future. I also think that some of the conclusions of our annual reports to Palo Alto and San Jose/Sunnyvale might be useful as perspective in the report.

5. You need to more explicitly present the big questions that should later be addressed by studies derived from the conceptual model. For example, "Were the POTWs a major source of metals in the past and how do they rank now?" "What is the recovery time in this system after sediments have been contaminated for a period; What is the recovery time from an episode of contamination?"

6. Studies of historical bathymetry changes accompanied by geochemical studies of sediment cores or marsh cores might be useful in deriving some of the information needs listed.

7. There are more important uncertainties than you list. While minor uncertainties should not be listed, some of the things mentioned above could be included with benefit.

3. Comments from Dr. Stephen Monismith

Review of Tetra Tech Conceptual Model Report

S. Monismith
Stanford University

General comments (given for Cu, but similar arguments would apply for Ni)

1. The overall synthesis of diverse elements, e.g. chemistry, hydrodynamics, hydrology, and data availability is quite good. My only complaint here is that more referencing could be done of where concepts, results or data come from, e.g., the sediment concentration time series, or the core concentration profiles. It should also be noted that some of these sources are in the peer-reviewed literature whereas others like my Asilomar presentation have not yet passed this level of quality control.

2. The figures and graphics are excellent and do help present the needed information.

3. (most important) In terms of doing balances on mass loading it is important to emphasize the methods used and uncertainties. Particular problems:

(a) As Jessie Lacy pointed out, the flux of dissolved Cu was not correctly computed in my original box model. After drawing up for myself a 3 box model (LSB, Dumbarton to SB Shoal, and SB Shoal to BB), I became convinced that if the mass exchanges between the second and third box and between the third box and the Central Bay are rapid, then the residence time Ed Gross computed mostly reflects the exchange between the first two boxes. This means that the net flux will be equal to the difference in concentration times the volume of LSB divided by the residence time. So to re-examine the question of dissolved Cu flux, I used the data presented in your report and aggregated the means:
(BB30 1.6ppb) + (BB15 2ppb) + (BA40 2.3 ppb) gives 2.0 ppb
(BA0 3.0 ppb) + (BA10 3.4ppb) gives 3.2 ppb

So the difference in concentration is 1.2 ppb, which with 20 day residence time and 8×10^7 m^3 volume in LSB, gives a flux of about 4.8 kg/day or 1750 kg per year, i.e., much less that before, and of the same order of magnitude as the POTW flux. Going through the same exercise for Ni, I get around 2040 kg/y. We (Jeremy Bricker) can probably do a little better by taking the real gradients and using Ed Gross's computed values of the longitudinal dispersion coefficient. Interestingly, the raw monitoring data do not should this trend of decreasing concentration nearly so clearly as do the means over all data. It should be noted that our residence time estimates are only valid dry weather. Clearly the lack of data on what happens in wet weather is an important shortcoming of the existing data.

(b) The Cu loading due to resuspension is very uncertain since all that I did was to choose sediment parameters (sinking velocities etc.) that gave sediment concentration values in the water column that look like those Dave Schoelhammer has measured at channel marker 17 in LSB. A major conceptual difference between what I did and what might actually happen is that I assumed sediment resuspension due to tidal currents in the channel, whereas in reality we might be seeing only the effects of wind wave resuspension in the shoals. We have no information whatsoever as to what the shoal-channel transfer of sediment, and hence sorbed Cu, might be. I would cite this as a significant impediment to assessing or modeling the effects of sediment dynamics on the mass balances of Cu. In fact, there is essentially no sediment or hydrodynamic data on what happens in the shallows south of the Dumbarton. I would rate this as an important limitation to trying to do the TMDL. We also do not have any real data on sediment rheology parameters like erodability; these could be gained in various ways like the VIMS sea carousel flume or other similar devices.

(c) Finally, in thinking about the non-point source (NPS) loading, it becomes apparent that how it enters the system is important. If it is "dirtier" than existing sediment when it enters the system, it will contribute to the dissolved Cu pool, whereas if it is cleaner, it will not. For example, re-running my box model with the NPS loading purely sorbed at observed partioning (which amounts to computing how much sediment needs to enter to give the estimated Cu load), reduces dissolved Cu concentrations the model predicts substantially.

4. In light of San Jose's remarkable Cu time series data, which I saw for the first time at our meeting, the conceptual model that gets built probably needs to differentiate according to dry and wet seasons. This is also important with regards to seasonality in the NPS loading of Cu and of sediment. Because of the difference in sediment dynamics between shallow and deep water, it may also need to treat shallow areas and channels separately.

5. Somehow, several of the major salient features of the existing data set don't come through strongly:
   (a) According to Sam Luoma, there used to be a linkage of bivalve tissue Cu burden and POTW loading; now the linkage is to river flow. I gather this may indicate that observed Cu concentrations may have little to do with POTW loading.
   (b) The annual cycle of Cu variability coupled with the weak spatial variability south of the Dumbarton also suggest that something other than passive scalar mixing of POTW Cu is involved.

6. When thinking about sediment dynamics, an analysis of long-term bathymetric changes like those the USGS has recently carried out in North Bay would be helpful for trying to infer whether or not the sediments are a significant source of Cu. This is a relatively straightforward thing to do.

1. Review Comments from Dr. Janet Hering

From: Janet Hering [jhering@its.caltech.edu]From: Janet Hering [jhering@its.caltech.edu]
Sent: Monday, May 17, 1999 12:01 PM
To: Grieb, Tom -- Tt, Inc.
Cc: jhering@cco.caltech.edu
Subject: Re: Report on the Technical Review of the Conceptual Model

Hi Tom, I looked through the (draft) Report on the TRC Review. Overall, I think this a very fair and accurate summary. I have just a few specific comments.

p. 2 -- typo in section 2.2 ("model" on wrong line)
p. 3 -- I think it might be a good idea to mention the issue of seasonality (and/or seasonal cycles) explicitly in both sections 2.2.1 and 2.2.2
p. 8 -- I think the review process could be improved by focusing the discussion at the TRC meeting on specific issues. I'm not a big fan of conference calls but perhaps that, in combination with some written communications between the TRC members and TMDL work group, would be helpful. I think you might ask the TRC to comment (in writing) on their perceptions of the main strengths and weaknesses of the report and to identify questions for discussion. I don't think it's necessary to present an overview of the material that the TRC has reviewed but I do think it's important that the TMDL workgroup put together a more complete and organized set of questions for the TRC to address.

Hope this helps. Janet

Prof. Janet Hering
California Institute of Technology
1200 E. California Blvd.
Environ. Eng. Sci. (138-78)
Pasadena, CA 91125
(tel) 626-395-3644
(FAX) 626-395-2940
(e-mail) jhering@its.caltech.edu
(web) http://vayu.che.caltech.edu/~ees/Hering.html

2. Review Comments from Dr. Sam Luoma

From: snluoma@usgs.gov
Sent: Friday, June 11, 1999 3:20 PM
To: Grieb, Tom -- Tt, Inc.
Subject: Re: Conceptual Model Review

Tom,
Sorry to be so slow in replying. I think the report covers things well. However, I would like to add to the research needs, the need to begin to study factors controlling the fate, bioavailabililty and effects of nickel. Our knowledge of copper is not complete, but nickel is an example of an element about which we know almost nothing in terms of its biological impacts. One of the biggest questions is how do natural inputs influence effects, as compared to inputs from urban runoff and the POTWs.
Cheers,
Sam

3. Review Comments from Dr. Stephen Monismith

From: Stephen Monismith [monismit@cive.Stanford.EDU]
Sent: Friday, June 11, 1999 9:06 AM
To: Grieb, Tom -- Tt, Inc.
Subject: Re: Report on the Technical Review of the Conceptual Model

Tom: The tech review document looks fine - I look forward to seeing the revised version of your report.
Stephen

Stephen Monismith
Director, Environmental Fluid Mechanics Laboratory
Associate Professor
Dept of Civil Engineering
Stanford University
Stanford, Ca. 94305-4020
(650) 723-4764